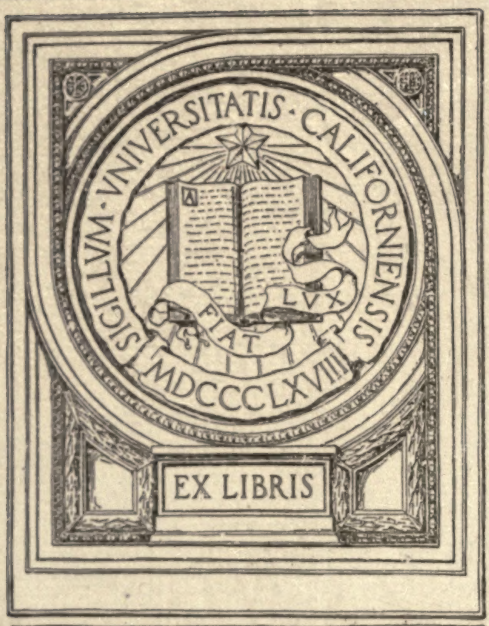

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INDUSTRIAL CHEMISTRY

A MANUAL

FOR USE IN TECHNICAL COLLEGES OR SCHOOLS

AND FOR MANUFACTURERS ETC.

BASED UPON A TRANSLATION (PARTLY BY DR T. D. BARRY)

OF STOHMANN & ENGLER'S GERMAN EDITION

OF

PAYEN'S 'PRÉCIS DE CHIMIE INDUSTRIELLE'

Anselme Payen

EDITED THROUGHOUT

AND SUPPLEMENTED WITH CHAPTERS ON THE CHEMISTRY OF THE METALS &c.

BY

B. H. PAUL, PH.D.

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PREFACE.

ONE of the most noteworthy characteristics of the present time is the growing recognition of science as the highest form of practical knowledge, and of the fact that, since the processes of industrial art are but particular instances of the general habitudes of nature, the successful conduct of technical operations, no less than the improvement of particular branches of industry, involves acquaintance with natural facts and principles, which it is the special business of abstract science to deal with altogether apart from considerations of utility.

In this respect no branch of science is more important than Chemistry, because there is scarcely any great industry in which the materials operated upon are not, at some stage or other, made to undergo chemical alteration. In the extraction of the useful metals from their ores, in the making of glass and pottery-ware, in dyeing and calico-printing, as well as in the preparation of various articles of food, such as bread, beer, etc., the desired results are obtained by producing suitable chemical alterations.

The various branches of industry involving a knowledge of Chemistry are moreover of such vast national importance that, while special practical experience is essential for their conduct, some general acquaintance with them is calculated to be useful to those not directly engaged in such pursuits; since the development or modification of old-established industries, as well as the introduction of new ones by the application of chemical discoveries, often determine radical and far-reaching changes that influence general commerce not less than particular departments of trade.

A knowledge of Chemistry is, therefore, to be regarded as one of the most essential qualifications of those engaged in manufacturing pursuits, and on this account it has long been made a subject of study in Continental schools. The desirability of adopting a similar course in this country is gradually becoming recognised, and it is believed that a work treating of the technical applications of Chemistry, in a concise and systematic manner, will be of service in promoting the general introduction of its study in schools and technical colleges.

From these points of view Payen's *Précis de Chimie industrielle* has been selected as the basis of this work, because it has always held a high position in France—where the study of Chemistry in its practical relations has long been systematically carried out—as well as in Germany—where the technical value of science is most of all appreciated and most successfully realised.

The systematic treatment of the subject in the original work has been rendered more complete by the addition of several chapters on the general chemistry of the metals and metallurgical operations, as well as several other branches of industry not dealt with in the French or German editions; so that the book will serve as a manual of Chemistry no less than as a source of information as to the nature of particular industrial operations.

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INDUSTRIAL CHEMISTRY.

GENERAL INTRODUCTION.

Nature of Chemical Phenomena.—In most of the operations of nature and art there is some obvious alteration of the material substances concerned in them. Such phenomena are the sensible manifestations of the activity inherent in all substances, and they are of two kinds. Thus, for instance, a bar of iron, when sufficiently heated, changes colour and becomes luminous: a mass of lead, under similar conditions, becomes liquid; and a lump of sugar placed in water gradually disappears, communicating its sweet taste to the water. Otherwise than in those particulars, however, the several substances remain unaltered in all these instances: although the heated iron is red, luminous, and softer than it was before being heated, it is just as much iron; while the liquid lead is essentially the same substance that it was before being melted. So, likewise, the solution of sugar in water is, like most other cases of simple solution, a phenomenon in which the alteration of either substance extends only so far as is indicated by the sugar becoming liquid and the water sweet; with these exceptions, both substances maintain their individuality, and they may be separated by simply evaporating the water, when the sugar will remain behind unchanged in quantity or in any of its characters. Phenomena of this kind are termed Physical in the more restricted sense of the word, and their consideration belongs to the science of Physics.

But a more radical alteration of material substances is the specially characteristic feature of many phenomena. Thus, when iron is exposed to the air, it becomes coated with a reddish crust, which gradually becomes thicker, and after a sufficient length of time the entire mass of the iron is converted into a red substance. Again, when a lump of sugar is suddenly heated, it melts, assumes a dark colour and swells up, giving off a quantity of vapour, until at last there remains a black coaly mass. The alteration in both instances is of such a nature that the distinctive characters of the original substances totally disappear and what remains is, in each case, not iron or sugar.

The changes that take place in the rusting of iron and in the charring of sugar serve to illustrate, in a general way, the nature of chemical action, and of the phenomena which are termed Chemical, in contradistinction to Physical or Mechanical phenomena, that do not involve any such radical alteration of material substances. The peculiar characteristic of chemical phenomena is the production of substances altogether different from those concerned in their formation. In this respect the effect of chemical action differs essentially from that of mere mechanical mixture or separation. Thus, for instance, if powdered sulphur be intimately mixed with very finely divided iron filings until the mixture appears to the eye as a perfectly uniform grey powder, there is still no alteration of the two substances beyond intermixture. The particles of sulphur and iron may be seen by the aid of a powerful microscope, and they may even be separated mechanically by mixing some of the powder with alcohol, and stirring with a magnet, to which the particles of iron will adhere, leaving the sulphur as a yellow powder. The separation may also be effected by digesting the powder with some liquid that dissolves sulphur without acting upon iron or the reverse.

If, however, some of the mixed powder be heated on an iron plate, it becomes incandescent, cakes together, and assumes a darker colour. After this has taken place, it is no longer possible to recognise distinct particles of iron and sulphur in the mass that remains, nor is it possible to separate those substances as before by any of the means above described. In fact, the substance that remains is neither iron nor sulphur: the alteration of these substances, as a result of chemical action, being of such a nature that both the sulphur and the iron disappear as such, and another substance distinct from both of them is produced. In all cases of chemical action there is such a positive metamorphosis of material substances, and phenomena of this kind constitute the subject-matter of chemical science.

Many phenomena connected with agriculture, animal nutrition and domestic economy, as well as many of the processes of manufacturing industry, are essentially chemical; hence the successful conduct of various operations of the Industrial arts presupposes an acquaintance with the general principles of Chemistry as well as special practical experience.

Definition of Chemistry.—In conformity with the distinction already pointed out as existing between physical and chemical phenomena, Chemistry may be defined as that branch of physical science which treats of the nature and relations of material substances, as regards their constitution and the metamorphoses of which they are susceptible. The extension of this knowledge and the elucidation of general principles by research, altogether apart from considerations of utility, constitute the special object of abstract chemistry. The object of technical chemistry, on the contrary, is the practical application of chemical knowledge for particular purposes and its utilisation, either in explaining the chemical processes that take place in various cases, or in modifying those processes to answer particular ends. It is from the latter point of view that the subject will be dealt with in detail in the following pages; but it is desirable, in the first place, to describe some of the characters most intimately connected with the physical constitution of substances, and to give a brief *résumé* of the general principles of Chemical Science.

PHYSICAL CHARACTERS OF SUBSTANCES.

The individuality of different substances is indicated to our senses by certain definite associations of characters, which are intimately connected with the constitution or special nature of the particular substances to which they belong.

The physical characters of substances are therefore of great interest to the chemist, since they serve to distinguish a great number of substances from each other. Among the most important are the state of aggregation, density or the relation of weight and volume; colour, expansion, fusibility, and other relations to light and heat; solubility, odour, taste, etc.

State of Aggregation.—The physical condition—solid, liquid, or gaseous—which a substance presents under certain conditions, is often an important distinctive character.

Some substances are ordinarily known only in a single state of aggregation: for instance, lime and carbon as solids; atmospheric air, hydrogen, etc., as gases. Other substances are known in two states of aggregation, as, for instance, alcohol in the liquid and gaseous states, platinum in the solid and liquid states. But many substances are capable of assuming all three of these conditions. Sulphur, for instance, under ordinary conditions a solid substance, may be melted by means of heat and converted into the liquid state, and by further heating made to assume the gaseous state. The same holds good with water, which—under ordinary conditions a liquid—may be converted by abstraction of heat into the solid state—ice, and by heating into the gaseous state—steam.

Certain physical characters, such as hardness, crystalline form and structure, etc., appertain specially to the solid state; fluidity or internal mobility is a common character of the liquid and gaseous states; and a high degree of expansibility is characteristic of the gaseous state.

In each of these states substances are capable of being subdivided to an extent far exceeding the power of observation; but since the occupation of space denoted by the term extension is inseparable from the idea of substance and inconsistent with infinite divisibility, substances are regarded from a physical point of view as being constituted of extremely minute particles or molecules, and the activity that is, in some form or other, a general character of natural substances, is regarded as appertaining to these ultimate particles or molecules, the constitution or internal structure of different substances as well as various other physical phenomena being determined by the varied exercise of this inherent activity.

The internal consistence of a solid or a liquid is indicative of a cohesive action between the molecules or ultimate particles of individual substances. This action is greatest in solids, less in liquids, and almost nothing in gases.

The cohesion of different substances varies very considerably, as is indicated by the degree of resistance which they offer to tearing, breaking, or disintegration; and the characters of toughness, brittleness, malleability, etc., as well as the diversity of internal structure indicated by differences in the surfaces of fracture of solids, and by the degree of viscosity of liquids, are results of the varied exercise of molecular action. Crystallisation is one of the most remarkable modes in which the exercise of force is manifested as influencing the internal structure of many solid substances. The regular geometrical forms which crystallisable substances are capable of assuming are often sufficiently characteristic to be of considerable assistance in distinguishing such substances from each other: thus, for instance, the crystals of ordinary nitre are hexagonal prisms, while those of the corresponding substance called sodium nitre are cubes.

Density: Specific Gravity.—Substances differ considerably as regards density, or the ratio of quantity to volume denoted in ordinary language by the terms heavy and light. Thus, for instance, gold is called a heavy substance, cork a light substance; the one sinks in water since its density is greater, the other floats because its density is less than that of water; but both substances sink with equal facility through air, the density of which is very considerably less than that of water or of cork. Platinum and hydrogen furnish an extreme illustration of the differences existing in respect to density, the one being nearly 24,000 times as dense as the other. The density of a substance is also a character that is constant under like conditions, and therefore it often serves the purpose of identification in conjunction with other characters.

Equal volumes of different substances necessarily differ in weight proportionately to their difference in density; and the numerical expression of the relative weights of substances, as compared with some standard, is termed their specific gravity. Water is generally taken as the standard of comparison for liquids and solids; while the standard for gases is either atmospheric air or hydrogen.

The cubic inch of water weighs under normal conditions of temperature and atmospheric pressure 252·5 grains, and this is the unit to which specific gravities are referred according to the English system; and the differences in specific gravity are expressed in thousandths. Thus, a cubic inch of sulphuric acid weighs 465·62, and consequently its specific gravity is 1·848—

$$252{\cdot}5 : 465{\cdot}62 = 1{\cdot}000 : 1{\cdot}848.$$

According to the French system of weights and measures, in which the litre is the unit of volume and the gram the unit of weight, the hundredth part of a litre of water weighs 1 gram at 4° C. and the weight of a cubic centimetre of any other substance expressed in grams is also the specific gravity of the substance.

Practically considerable use is made of specific gravity. From the specific gravity of liquids containing various substances in solution, the amounts of such substances may be ascertained. Water containing another substance dissolved in it is rendered specifically heavier or lighter according to the nature of the dissolved substance. If the substance dissolved be specifically lighter than water, the specific gravity of the solution is reduced; as, for instance, in the case of a mixture of alcohol and water. The specific gravity is increased when the substance dissolved is specifically heavier than water, as, for instance, in the case of a solution of salt or a mixture of sulphuric acid and water. In the same way the specific gravity of water is increased or reduced by the solution of gases. The specific gravity of a solution of ammonia is less than that of water, while that of a solution of hydrochloric acid gas is greater.

A very convenient instrument for determining the specific gravity of liquids is the hydrometer, which consists of a hollow globe or cylinder, with a stem constructed so as to float upright when immersed in a liquid. The volume and weight of the instrument are so regulated that it sinks in water either to the point A or A′ according as it is required to indicate the specific gravity of liquids specifically heavier or lighter than water, and the points to which the hydrometer sinks in liquids of various specific gravity are indicated upon the stem, either by figures corresponding to actual specific gravity or by arbitrary degrees. If such an hydrometer be placed in a liquid, the specific gravity can be at once read off. An instrument of this kind is, however, only serviceable for a definite temperature, because the specific gravity of liquids alters with the temperature.

Hydrometers are also constructed so as to indicate directly the amounts of particular substances in mixtures or solutions: *e.g.* the alcoholometer for determining the alcoholic contents of a liquid, the saccharimeter for determining the saccharine contents of solutions of sugar, etc.

Melting Point: Boiling Point.—Every solid body that is capable of assuming a different state of aggregation must, for its conversion into the liquid condition, be raised to a temperature peculiar to itself: this temperature is termed the melting point of the substance. In like manner every liquid for its conversion under the ordinary atmospheric pressure into the gaseous state, must be raised to a temperature peculiar to itself, and this temperature is termed the boiling point of the liquid.

The state of aggregation of substances is influenced not only by heat, but likewise by the pressure to which they are subject. For instance, if a vessel containing water be placed under the receiver of an air-pump, and the atmospheric pressure upon the surface of the water is reduced by pumping out the air, the water will boil and assume the gaseous condition at the ordinary temperature. On the other hand, a gas may be converted, by means of pressure, into the liquid state. Quite recently hydrogen, oxygen, and nitrogen, which have hitherto been regarded as permanently gaseous, have been liquefied, and probably all gases admit of being thus converted by pressure into the liquid or the solid condition.

Specific Heat.—Equal quantities of different substances require unequal quantities of heat to raise their temperature equally.

By the specific heat of a substance is understood the relative amount of heat which it requires in order to produce a certain increase of temperature. The quantity of heat requisite for raising the temperature of a kilogram of water from 4° to 5° Cent. is taken as the unit, and this is termed the heat-unit.

The quantity of heat requisite to produce an equal increase of temperature in a kilogram of mercury is only 0·033 of the heat unit, and this fraction expresses the specific heat of mercury relatively to water = 1·000; in other words, the same quantity of heat that raises the temperature of a kilogram of water one degree, Centigrade, would produce an equal increase of temperature in about 30 kilograms of mercury.

The heat unit, however, is not an absolute quantity; it varies according to the unit of weight and the thermometric scale to which it refers. According to British usage the heat unit is the quantity of heat that raises the temperature of a pound of water from 40° to 41° Fahrenheit. The kilogram being about $2\frac{2}{9}$ times as much as the pound, and the Centigrade degree 1·8 times the Fahrenheit degree, there is a proportionate difference between the British and French heat units.

British heat unit.		French heat unit.
1·	=	0·251996
3·96832	=	1·

Specific heat is of practical importance, for the quantity of heat requisite for raising the temperature of a definite weight of any substance can be calculated if the specific heat of the substance in question be known. The greater the specific heat is, the greater is the quantity of heat which has to be communicated to the liquid in order to raise its temperature to any given degree, and the less the specific heat the smaller is the quantity of heat which is requisite.

NATURE OF CHEMICAL ACTION.

If the experiments already mentioned as illustrative of the distinction between physical and chemical phenomena were made under such conditions that the weights of the substances could be ascertained both before and after the alteration produced in each case, it would be found that, while the iron bar weighed just the same after being heated as it did before, and while the weight of the solution of sugar in water was exactly equal to the joint weights of the sugar and the water used, considerable alterations of weight accompanied the chemical alteration of the iron in rusting and that of the sugar by charring it. The reddish substance resulting from the alteration of the iron would weigh nearly half as much again as the iron before it underwent that change. On the contrary, the black cinder left after heating the sugar would not weigh more than about one-third as much as the original sugar. Such alteration in weight is invariably recognisable when substances undergo chemical change, and it constitutes one of the most marked characteristics of chemical phenomena. By further examination, it would be found that in the rusting of iron another substance is added to the iron, and that this addition exactly accounts for the observed increase of weight. The substance thus added to the iron is oxygen, derived from atmospheric air, and the change that takes place consists in the union of these two substances, iron and oxygen, in such a way as to produce another substance quite distinct from either of them, just the same as, by heating the mixture of iron and sulphur previously mentioned, another substance is produced. Chemical change of this kind is termed combination.

By a similar examination of the other instance given as illustrating chemical change, it would be found that the substances given off as vapour on heating sugar would exactly make up the difference in weight between the cinder and the original sugar, and that the change consists in the resolution or breaking up of an individual substance into several other substances distinct from it. Chemical change of this kind is termed decomposition.

All substances are susceptible, under the influence of various conditions, of being transformed by chemical action in one or other of the modes just described, and by such means a vast number of substances may be produced from those actually met with in nature. Some of the most important operations of industrial art have for their object the production of such chemical alterations.

But though all material substances can be chemically altered either by decomposition or by combination, chemical research has led to the discovery of certain substances which are in so far peculiar that they cannot be decomposed by any known means. No one of the substances belonging to this class can be transformed into anything that is different, and at the same time less in quantity. The peculiarity of these substances consists in their being capable of chemical change only by combination with other substances; consequently, the chemical alteration of these substances is invariably attended with increase of weight, as in the rusting of iron. The alteration iron undergoes in rusting consists in combination with atmospheric oxygen; and as iron is a substance of the kind now referred to, it is only by such combination with some other substance that it undergoes chemical change. Some of the characters of iron may indeed be altered by various means: by very intense heating it may even be converted into a liquid state; it may also be rendered magnetic; and it may be reduced to such an extremely minute state of subdivision as to appear an impalpable black powder; but in all these cases the alteration is merely of that kind already described as physical and affecting only the internal structure of the substance; the quantity of material is neither increased nor decreased, the essential nature of the substance remains unaltered: and even in the minute particles of the black powder the distinctive characters of metallic iron may be recognised by the aid of the microscope.

Substances of this kind, which cannot be decomposed, are therefore termed simple substances, in contradistinction to compounds, or those substances which are capable of being decomposed. All substances of the latter class may, however, be resolved by chemical action into two or more simple substances; and, for this reason, the simple substances are, from a chemical point of view, regarded as the primary materials or ultimate constituents of which all compound substances are made up. Hence they are termed elementary substances or chemical elements.

The elementary substances of modern chemistry are at least sixty-three in number, as detailed in the first column of the accompanying table, and the distribution of these elementary substances, under different conditions, is indicated by the asterisks in columns 4 to 13.

Only a few of the elementary substances occur naturally in the free state, as it is termed in chemical language, when they are uncombined with other substances (see column 11 of the table). The greater number of them are always met with in various states of combination with each other. However, the compounds of the several elementary substances occurring naturally are not, generally speaking, very numerous as compared with the multiplicity of compound substances that can be obtained artificially by various methods of chemical treatment.

Some of the chemical elements are extremely rare, and the substances containing them are of little or no importance for practical purposes; but some others, on the contrary, are of very general occurrence, either in the free state or as constituents of some of the most abundant and most important materials concerned in the chemical phenomena of nature and of industrial art. These latter are thirty-five in number, and they are distinguished in the table by the large type in which their names are printed. Out of these thirty-five elementary substances there are eighteen, indicated by the asterisks in the fourth column, which occur very abundantly and very frequently in all kinds of materials belonging to the mineral kingdom. The thirteenth column shows that precisely the same eighteen elementary substances are distributed throughout the materials originating from plants and animals. Only four of these elementary substances—carbon, oxygen, nitrogen, sulphur—occur naturally to any considerable extent in the uncombined state.

Relatively the greatest number of elementary substances occur in mineral veins or lodes, where nearly all the more rare elementary substances are found, excepting those associated with platinum (see column 8). In granite rocks, also, there is a very general distribution of elementary substances (column 7), while in basaltic and volcanic rocks the number of elementary substances is smaller (see columns 5 and 6).

The elementary substances that have been found in the melted masses of lava, and

1	2	3	4	5	6	7	8	9	10	11	12	13
Aluminum	Al	27·4	*	*	*	*	*	*	*	—	*	*
Antimony	Sb	122	—	—	—	—	*	—	—	*	—	—
Arsenic	As	75	—	—	*	*	*	*	*	*	—	—
Barium	Ba	137	—	—	—	—	*	*	—	—	—	—
Bismuth	Bi	210	—	—	*	*	*	—	—	—	—	—
Boron	B	11	—	—	—	*	*	*	*	—	—	—
Bromine	Br	80	*	—	—	—	*	*	—	—	—	*
Cadmium	Cd	112	—	—			*	—	—	—	—	—
Cæsium	Cs	133										
Calcium	Ca	40	*	*	*	*	*	*	*	—	*	*
Carbon	C	12	*	—	—	*	*	*	*	⊛	*	*
Cerium	Ce	138	—	—	—	*	*	—	—	—	—	—
Chlorine	Cl	35	*	*	*	*	*	*	*	—	*	*
Chromium	Cr	52	—	—	*	*	*	—	—	—	*	—
Cobalt	Co	59·8	—	—	*	*	*	*	—	—	*	—
Copper	Cu	63·4	—	—	*	*	*	*?	*	*	*	
Didymium	Di	95	—	—	—	*	*	—	—	—	—	—
Erbium	Eb	168·9										
Fluorine	Fl	19	*	*	*	*	*	*	—	—	—	*
Glucinum	G	9·4				*	*					
Gold	Au	197	—	—	*	*	*	—	—	*	—	—
Hydrogen	H	1	*	*	*	*	*	*	*		*	*
Indium	In	113·4										
Iodine	I	127	*	—	—	—	—	*	—	—	—	*
Iridium	Ir	198	—	—	*	—	—	—	—	*	—	—
Iron	Fe	56	*	*	*	*	*	*	*	—	*	*
Lanthanum	La	93·6	—	—	—	*	*	—	—	—	—	—
Lead	Pb	207	—	—	*	*	*	—	*	*	*	—
Lithium	L	7	—	—	—	*	*	*	—	—	—	—
Magnesium	Mg	24	*	*	*	*	*	*	—	—	*	*
Manganese	Mn	55	*	*	*	*	*	*	*	—	*	*
Mercury	Hg	200	—	—	—	—	*	—	—	*	—	—
Molybdenum	Mo	96	—	—	—	*	*	—	—	—	—	—
Nickel	Ni	59	—	—	—	—	*	—	—	—	*	—
Niobium	Nb	94	—	—		*	*	—	—	—	—	—
Nitrogen	N	14	*	—	—	—	—	*	*	⊛	*	*
Osmium	Os	199·2	—	—	*	—	—	—	—	*	—	—
Oxygen	O	16	*	*	*	*	*	*	*	⊛	*	*
Palladium	Pd	106·5	—	—	*	*?	*	—	—	*	—	—
Phosphorus	P	31	*	*	*	*	*	*	—	—	*	*
Platinum	Pt	197·1	—	—	*	—	*	—	—	*	—	—
Potassium	K	39	*	*	*	*	*	*	*	—	*	*
Rhodium	Rh	104·4	—	—	*	—	—	—	—	*	—	—
Rubidium	Rb	85·4										
Ruthenium	Ru	104·4	—	—	*	—	—	—	—	*	—	—
Selenium	Se	80	—	—	—	—	*	—	*	*	*	
Silicon	Si	28·5	*	*	*	*	*	*	*	—	*	*
Silver	Ag	108	—	—	—	*	*	—	—	*	—	—
Sodium	Na	23	*	*	*	*	*	*	*	—	*	*
Strontium	Sr	88	—	—	—	—	*	*	—	—	—	—
Sulphur	S	32	*	*	*	*	*	*	*	⊛	*	*
Tantalum	Ta	182	—	—		*	*	—	—	—	—	—
Tellurium	Te	128	—	—	—	—	*	—	—	*	—	—
Thallium	Tl	204										
Thorium	Th	231·5	—	—	—	*	—	—	—	—	—	—
Tin	Sn	118	—	—		*	*	—	—	—	—	—
Titanium	Ti	50	—	*	*	*	*	—	—	—	—	—
Tungsten	W	184				*	*					
Uranium	U	240	—	—	*	*	*	—	—	—	—	—
Vanadium	V	51·3	—	—	—	—	*	—	—	—	—	—
Yttrium	Y	92	—	—	—	*	*	—	—	—	—	—
Zinc	Zn	65	—	—	*	*	*	—	—	—	—	—
Zirconium	Zr	89·5	—	—	—	*	*	—	—	—	—	—

in the various other solid, liquid, and gaseous materials, ejected from the interior of the earth during volcanic eruptions (see column 10), as well as in the water of mineral springs rising from very great depths (see column 9), are the same as those existing in rock at and near the earth's surface (see columns 4, 5, 6, and 7): hence it is inferred that the material of the earth is in this respect the same throughout. The chemical nature of volcanic products admits, moreover, of the conclusion that in the interior of the earth, with some few exceptions, the elementary substances exist, in the same relative proportions and in the same states of combination as at the surface.

Column 12 indicates the elementary substances that have been found in meteorites.

Classification of Elementary Substances.—The elementary substances are commonly classified as metals and metalloids, according to their physical characters in the uncombined state, and partly also, on account of their relations in a chemical point of view. The metals most generally known are, with the single exception of mercury, solid under ordinary conditions: they are absolutely opaque and present a peculiar lustre or brilliancy that may be increased by polishing. Another physical character, which, in combination with those already mentioned, has been regarded as most distinctive of metallic substances, is an internal mobility, in virtue of which the shape of a mass of metal may be altered by pressure, hammering, or other mechanical means, without disintegration or disruption of the substance. This character is expressed by the terms malleability—denoting a capability of flattening or spreading out under the hammer or between rollers—and ductility—denoting a capability of lengthening, and becoming thinner by stretching or being drawn through a hole of less area than the transverse section of the piece of metal. Metals are also excellent conductors of heat and electricity. In regard to these characters, however, the metals present marked differences of degree, and some of the elementary substances comprised among metalloids also differ only in degree from those popularly known as metals. The distinction is, therefore, to a great extent arbitrary, and so far as such characters are concerned the classification of certain elementary substances as metalloids merely signifies that those substances resembling metals, in so far as they are elementary, possess in a less marked degree the characters distinctive of metals.

Metalloids.	Metals.		
Oxygen	Hydrogen	Cobalt	Copper
Sulphur	Potassium	Nickel	Lead
Selenium	Sodium	Uranium	Thallium
Tellurium	Lithium	Iron	Indium
	Cæsium	Chromium	
Chlorine	Rubidium		Mercury
Bromine		Tin	Silver
Iodine	Barium	Titanium	Gold
Fluorine	Strontium	Zirconium	Platinum
	Calcium	Thorium	Palladium
Nitrogen		Molybdenum	Rhodium
Phosphorus	Aluminum	Tungsten	Ruthenium
Arsenic	Glucinium	Niobium	Osmium
	Yttrium	Tantalum	Iridium
Carbon	Erbium	Vanadium	
Boron	Cerium	Antimony	
Silicon	Lanthanum	Bismuth	
	Didymium		
	Magnesium		
	Zinc		
	Cadmium		

The difference between metals and metalloids in regard to chemical characters and relations is manifested chiefly in the functions which the substances of one or the other class perform in their compounds. Probably all elementary substances are capable of existing in a state of combination with each other in pairs; but as a rule this capability is greater in proportion to the difference between the elementary substances. Thus, for instance, compounds of the metals with each other possess far less stability and individuality than the compounds of metals with oxygen or sulphur, chlorine, &c., and they present greater resemblance to mere mechanical mixtures than compounds of the latter class, which generally possess characters totally different from those of their constituents in the uncombined state. This is also the case, to some

extent, with the compounds of certain metalloids with each other, though as a rule the metalloids have a greater capability of forming definite and distinct compounds with each other than the metals have.

Combining Proportions.—In compound substances possessing chemical individuality, the elementary substances of which they consist, always bear a definite quantitative ratio to each other by weight, which is constant for any particular substance under all conditions in which it is capable of existing. Thus in the case of water, which is a compound of oxygen with hydrogen, the ratio of these elements is as 8 : 1 by weight. The same ratio of elementary constituents obtains in ice and steam, which are merely different molecular forms of the same substance. In chemical action also similar definite relations are always recognizable between the weights of the original substances and the weights of those produced from them either by combination or by decomposition. When oxygen unites with hydrogen to form water it is always in the proportion of 8 : 1 by weight, and whenever water is decomposed the hydrogen produced amounts to $\frac{1}{9}$ of the water decomposed, while the oxygen produced at the same time amounts to eight times the quantity of the hydrogen by weight.

The existence of such definite relations of weight among the substances concerned in chemical changes, and between the constituent elements of compound substances, has already been mentioned as one of the most important features of chemical phenomena, and the investigation of this general fact has led to the establishment of the fundamental principle of chemical science, that the elementary substances combine with each other only in definite proportions by weight, the ratio of the elementary constituents of any given substance being constant.

While in water hydrogen is always combined with eight times its weight of oxygen, in hydrochloric acid it is combined with 35·5 times its weight of chlorine, in hydrobromic acid with 80 times its weight of bromine, in hydriodic acid, with 127 times its weight of iodine, in sulphuretted hydrogen, with 16 times its weight of sulphur, in ammonia, with 4·67 times its weight of nitrogen, and in marsh gas, with 3 times its weight of carbon.

Again in the compound of oxygen and chlorine to which the peculiar characters of bleaching powder are due, a quantity of oxygen, equal to that which combines with one part of hydrogen to form water, is combined with 35·5 parts of chlorine, and in carbonic acid gas an equal quantity of oxygen is combined with three parts of carbon. In common salt a quantity of chlorine equal to that which combines with one part of hydrogen to form hydrochloric acid is combined with 23 parts of sodium, and in sodium oxide the proportion of sodium to oxygen is as 23 : 8.

These quantities of oxygen, chlorine, etc., are relatively to hydrogen the combining proportions of those elementary substances, and since they exactly replace each other in certain compounds they are termed equivalent proportions.

The relations of the elementary substances to each other in this respect may therefore be expressed by numbers representing the relative proportions by weight in which these substances combine or otherwise take part in the various kinds of chemical change; and if such numbers represent the proportions in which the several substances combine with the unit of hydrogen or with the quantity of oxygen equivalent to it, they will also represent the proportions in which those substances combine with each other or act chemically upon each other, as shown below:—

Hydrogen	1
Oxygen	8
Chlorine	35·5
Bromine	80
Iodine	127
Sulphur	16
Sodium	23
Silver	108

Thus hydrogen and chlorine combine in the proportions of 1 to 35·5; hydrogen and sulphur in the proportions of 1 to 16; chlorine and silver in the proportions of 35·5 to 108; chlorine and sodium in the proportions of 35·5 to 23; oxygen and silver in the proportions of 8 to 108, and so on.

In the combination of substances which are themselves compound the same rule obtains, and the equivalent of a compound substance is the sum of the equivalents of its constituents. Thus the equivalent of hydrochloric acid is $36{\cdot}5 = 35{\cdot}5 + 1$; the equivalent of sodium oxide is $31 = 23 + 8$, and when hydrochloric acid reacts with sodium oxide it is in the proportion of 36·5 to 31; when hydrochloric acid reacts with silver oxide it is in the proportions of 36·5 to 116.

In many cases, however, the elementary substances are capable of combining with

each other in more than one proportion; for example, there is besides water another compound of hydrogen with oxygen, containing a larger amount of oxygen than water does: there are also two compounds of carbon with oxygen, in which the amounts of oxygen are severally 57·14 and 72·72 per cent., and there are two compounds of iron with oxygen, containing respectively 30 per cent. and 22·22 per cent. of oxygen. But the ratios of the elementary constituents in these compounds bear very simple relations to each other; the proportions of the constituents in one compound being simply multiples or submultiples of the proportions in which these constituents are combined in another compound of them. Thus, in the two compounds of hydrogen the ratios are as 8 : 1 and as 16 : 1, the one containing relatively to the hydrogen exactly twice as much oxygen as the other does. In the two compounds of carbon with oxygen, also, the ratios of the constituents are respectively as 3 : 8 and 6 : 8, the one containing relatively to oxygen just twice as much carbon as the others. In one of the compounds of iron with oxygen the ratio of the constituents is as 28 iron to 8 oxygen, while in the other it is as 18·67 iron to 8 oxygen, or $28 \times 2 : 8 \times 3 = 56 : 24$.

This fact is well illustrated by the compounds of nitrogen with oxygen, of which there are five, as follow:

	Nitrogen		Oxygen			
$4{\cdot}67 \times 3$	= 14	:	8			Nitrous oxide
$4{\cdot}67 \times 3$	= 14	:	16	=	8×2	Nitric oxide
	4·67	:	8			Nitrous anhydride
		or				
	14	:	24	=	8×3	
$4{\cdot}67 \times 3$	= 14	:	32	=	8×4	Peroxide of nitrogen.
$4{\cdot}67 \times 3$	= 14	:	40	=	8×5	Nitric anhydride.

Here it will be seen that the quantities of oxygen combined with nitrogen in the last four substances are, relatively to the nitrogen, in the proportions of two, three, four, and five times as much as is combined with the unit of hydrogen in water, or with 14 parts of nitrogen in the first-named substance, the general expression of this fact being that when any elementary substance is capable of combining with another in several proportions, those proportions bear a simple multiple relation to each other.

A theoretical interpretation of the general fact that in all kinds of chemical change there are such definite and fixed relations of weight between the elementary substances, is furnished by the application of the atomic hypothesis of the constitution of material substances. For this purpose it is assumed that each elementary substance consists of extremely minute particles which are incapable of further subdivision, and are therefore termed atoms. According to this view, chemical change consists in the union or separation of the ultimate particles or atoms of different elementary substances, and the relations of weight observed in all cases of chemical change are due to the relative weights of the atoms of the particular elementary substances taking part in those changes. Thus, for instance, in the combination of hydrogen and chlorine, the weight of the chlorine is thirty-five and a half times as much as that of the hydrogen with which it unites; in the combination of hydrogen and bromine, the weight of the bromine is eighty times that of the hydrogen, and in the combination of hydrogen and iodine the weight of the iodine is one hundred and twenty-seven times that of the hydrogen. Taking hydrogen as the unit, the relative weights of the atoms of hydrogen, chlorine, bromine, and iodine will therefore be 1, 35·5, 80, and 127. This conclusion presupposes the assumption that in the combination of chlorine, bromine, or iodine with hydrogen, a single atom of each of these substances unites with a single atom of hydrogen, and that is the view adopted in regard to these elementary substances.

The numbers thus arrived at from a study of the chemistry of the several elementary substances, as representing the relative weights of their ultimate particles or atoms, are termed the atomic weights, and in the cases just mentioned the atomic weights coincide with the equivalents of the substances referred to. But there is not always this coincidence between the atomic weight and the equivalent of an elementary substance. Thus, for instance, in the combination of hydrogen with oxygen to form water, the weight of the oxygen is eight times as much as that of the hydrogen with which it unites; but a variety of considerations have led chemists to regard the relative weight of the atom of oxygen as being sixteen times as great as that of the hydrogen atom. According to this view, therefore, the molecule of water will consist of three atoms, viz., two of hydrogen united with one of oxygen. In like manner the compound of hydrogen and nitrogen contains 4·67 times as much nitrogen as hydrogen, but the relative weight of the atom of nitrogen is taken as being fourteen times as great as that of the hydrogen atom, and therefore the molecule of ammonia is represented as consisting of four atoms, viz., three of hydrogen united with one of nitrogen.

In marsh gas, again, hydrogen is combined with three times its weight of carbon; but as the relative weight of the atom of carbon is taken as being twelve times as great as that of the hydrogen atom, the molecule of marsh gas is represented as consisting of five atoms—viz., four of hydrogen united with one of carbon.

In other words, the chemical value or combining capacity of the atoms of the elementary substances is supposed to differ, and that the atoms of some of them are in this respect equivalent to two, three, or four, or even as many as seven hydrogen atoms; and this difference in the equivalent value of the atomic proportion of any elementary substance relatively to hydrogen generally extends through all its compounds: thus, for instance, the compounds of the bivalent elementary substance sulphur are generally bivalent also, as in the case of sulphuric acid, etc.

Those elementary substances which combine with each other in simple atomic proportions, like hydrogen, silver, chlorine, bromine, and iodine, are termed monatomic or univalent; those which combine with two atomic proportions of hydrogen or chlorine, like oxygen or sulphur, are termed diatomic or bivalent; those which combine with three atomic proportions of hydrogen or chlorine are termed triatomic or trivalent; while others are termed tetratomic or quadrivalent, pentatomic or quinquivalent, hexatomic or sexvalent, according to the number of atomic proportions of hydrogen that one atomic proportion of the respective elementary substances is equal to in combining capacity.

This difference in the chemical value of the atomic proportions of the several elementary substances is in some cases a constant characteristic of elementary substances; in other cases, however, the same substance is capable of exhibiting different relations of atomicity or chemical value as regards hydrogen and other substances: thus, for example, iron is in some compounds bivalent, in others quadrivalent or sexvalent; nitrogen in some compounds is trivalent, in others quinquivalent; molybdenum is in some compounds bivalent, in others quadrivalent, and in others sexvalent, while even chlorine and oxygen must be regarded in some compounds as being respectively septivalent and quadrivalent.

The numbers placed opposite to the several elementary substances in the third column of the table on page 6 represent the atomic proportions of the several elementary substances, and are termed the atomic weights, inasmuch as they are assumed in accordance with the atomic theory to represent the relative weights of their respective atoms.

Combination by volume.—In addition to the definite relations of weight existing among the substances concerned in all kinds of chemical change, there is, in the case of elementary substances that are gaseous, a further remarkable relation between the volumes of the combining proportions. For example, taking hydrogen gas as the unit of volume and of weight in comparing the densities and combining proportions of the elementary substances, the density of chlorine gas is to that of hydrogen gas as 35·46 : 1; and these numbers expressing the relative weights of equal volumes exactly coincide with the numbers representing the proportions by weight in which chlorine and hydrogen are chemically combined together in hydrochloric acid. In other words, the elementary constituents of any given quantity of hydrochloric acid would occupy exactly equal volumes when in the free state, under equal conditions of temperature and pressure. Again, the density of oxygen gas is to that of hydrogen gas as 16 : 1, and in water these elements are combined in the proportion of 8 : 1 by weight, consequently the volume of the hydrogen in this compound is to that of the oxygen combined with it as 2 : 1.

In like manner the density of nitrogen gas is to that of hydrogen gas 14 : 1, and as in ammonia these elements are combined together in the proportion of 4·67 : 1 by weight, the gaseous volume of the hydrogen in this compound is to that of the nitrogen combined with it as 3 : 1.

In the case of compound substances that are, under ordinary conditions, gaseous, or are capable of assuming the gaseous condition, and whose constituent elements are also gaseous, there are analogous simple relations between the gaseous volumes of the compound substances and the volumes of their constituents when in the free state, under equal conditions of temperature and pressure. Thus the density of hydrochloric acid gas is the mean of the densities of its constituents, and is to that of hydrogen as 18·25 : 1, since the volume of this gas is equal to the joint volumes of its constituents:

Hydrogen		Chlorine		Hydrochloric acid
1	+	35·5	=	36·5

In water the volume of the hydrogen is twice that of the oxygen combined with it,

and this substance in the state of vapour occupies the same volume as the hydrogen it contains:

Hydrogen		Hydr.		Oxygen		Water
| |	+	| |	+	| |	=	| | |
1	+	1	+	16	=	18

In this case therefore the combination of the elements is attended with a reduction of volume, or, as it is termed, condensation, amounting to one-third of the joint volumes of the constituents in the free state, and the density of water in the state of steam is to that of hydrogen as 9 : 1.

The volume of gaseous ammonia is equal to one-half the joint volumes of its constituents in the free state:

Hydrogen		Hydr.		Hydr.		Nitrogen		Ammonia
| |	+	| |	+	| |	+	| |	=	| | |
1	+	1	+	1	+	14	=	17

and consequently its density is to that of hydrogen as 8·5 : 1, as there is a condensation amounting to one-half the joint volumes of the constituents.

NOMENCLATURE AND NOTATION.

The technical language of Chemistry is of a twofold nature, comprising a system of naming substances according to their composition and a system of representing their composition by certain signs or symbols.

The nomenclature of the elementary substances is to a great extent arbitrary; and it would probably be impossible as well as useless to regulate it by any uniform principle.

The names by which many of the chemical elements are known date back to periods long antecedent to the recognition of the elementary nature of the substances they are now used to represent, as in the case of gold, silver, copper, iron, etc.; and in some instances certain of these names, such as mercury, sulphur, etc., had formerly a significance very different from what they now possess. Many of the more modern names of elementary substances, such as hydrogen, oxygen, chlorine, etc., are derived from Greek words denoting some characteristic properties of the several substances, or some circumstance connected with their occurrence. Thus the name hydrogen is derived from *ὕδωρ* water and *γεννάω* to generate, in reference to the fact that water is produced by the combustion of hydrogen. The name oxygen is derived from *ὀξύς* sour and *γεννάω* to generate, and it was adopted in reference to a premature assumption that the element it represents was a specific acidifying principle, since many of its compounds possess chemical characters analogous to vinegar. The name phosphorus again is derived from *φῶς* light and *φορέω* bear to, on account of the peculiar luminous appearance of the substance it represents. Lanthanum is so named from *λανθάνω* to lie hidden, because its oxide had for some time been confounded with that of another elementary substance (cerium); while didymium is so named from *δίδυμος* twin, in reference to its frequent association with lanthanum. The name chlorine is derived from *χλωρὸς* green, because of the greenish-yellow colour of this substance, and iodine is so named from *ἰοειδής* violet, on account of the colour of its vapour. The names of other chemical elements are derived from the names of the substances in which they were discovered, as aluminum from alum, potassium from potash; or from the names of places where the substances containing them were first found, as strontium from Strontian in Scotland, yttrium from Ytterby in Sweden. In some instances the names of elementary substances are more fanciful, as vanadium, derived from Vanadis, a Scandinavian deity.

The signs or symbols by which the elementary substances are represented are either the initial letters of their ordinary names, as in the case of carbon, hydrogen, and oxygen, or the initial letter of the Latin name, as in the case of potassium, the symbol of which is K (Kalium), or else the symbol is formed of the initial letter together with some other letter of the name, which serves best to make the symbol distinctive, as in the case of Chlorine Cl, Calcium Ca, Nickel Ni, Iron Fe (ferrum), Strontium Sr, Tin Sn (stannum), and Mercury Hg (hydrargyrum).

As regards compound substances, the object of systematic chemical nomenclature is not only to give them distinctive names, but at the same time to indicate by those names the elementary composition as well as the chemical nature of the substances they represent. Generally speaking, this is easily done in the case of substances containing only two or three elementary constituents; but the numerous compounds of carbon with hydrogen, oxygen, nitrogen, etc., are to a great extent exceptions to this rule, inasmuch as the constitution of these substances is often very complex.

For the purpose of classification, compounds consisting of two elementary substances, are named according to the elementary constituents which a number of them contain in common. Thus, for instance, compounds of oxygen with another substance are termed oxides; similar compounds of sulphur or phosphorus are termed sulphides or phosphides; and compounds of chlorine, bromine, or iodine are termed chlorides, bromides, or iodides, these names indicating the generic character of the substances.

In naming individual substances of this kind the names of the constituents of a particular substance are coupled together in such a way that while the name of one constituent is made to indicate the generic character of the compound, the name of the other constituent is used as an adjective to indicate its specific characters. Thus, for instance, water, which is a compound of hydrogen with oxygen, is termed hydric oxide, a compound of copper with oxygen is termed cupric oxide, and common salt, a compound of sodium with chlorine, is termed sodic chloride.

Substances composed of the same elementary constituents in different proportions are distinguished by adding a prefix to their generic or specific names, as the case may require, or by varying the termination of their specific names. Thus, for instance, the compound of hydrogen and oxygen, containing twice the proportion of oxygen that water does, is termed hydric dioxide, and the compound of copper with oxygen, containing twice the proportion of copper that cupric oxide does, is termed dicupric oxide. Again, two of the compounds of iron and oxygen are respectively named ferric oxide and ferrous oxide.

The symbols by which the elementary substances are represented indicate not only the nature of these substances but also a definite proportion of each substance, and compounds are represented by formulæ constructed by the juxtaposition of the symbols of their constituent elements. Thus, for instance, hydrochloric acid is represented by the formula HCl, which indicates that it is a compound of chlorine and hydrogen in the proportions of 35·5 to 1, and that the molecules of hydrochloric acid or the smallest particles into which it can be separated consist of an atom of chlorine united with an atom of hydrogen. When the molecules of a compound contain more than one atom of an elementary substance a small figure is placed against the symbol; thus water is represented by the formula H_2O, to show that the molecule consists of two atoms of hydrogen united with one atom of oxygen. In like manner ammonia is represented by the formula NH_3, sulphuric acid by the formula H_2SO_4, and caustic soda by the formula KHO.

These formulæ represent molecules of the respective compounds, while the symbols of the elementary substances represent atoms or the smallest quantities which unite chemically, and the molecules of elementary substances are represented as consisting of pairs of similar atoms, thus: HH, OO, NN, etc.

The chemical value or atomicity of an elementary substance is represented in formulæ by dashes or roman numerals placed against the symbol, thus: O'' S^{II} N^{III} C^{IV}.

Chemical change can be represented by arranging the formulæ of the substances concerned in the form of an equation; thus the decomposition of sulphuric acid by zinc is represented as follows:

$$H_2SO_4 + Zn = ZnSO_4 + 2H.$$

A chemical formula is intended to serve as an indication not only of the particular elementary substances contained in a compound, but also of their relative proportions; thus, for instance, the formula of water, H_2O, indicates that this substance is not only a compound of hydrogen and oxygen, but that it is a compound consisting of two atomic proportions of hydrogen united with one atomic proportion of oxygen. Chemical formulæ are therefore to some extent a means of expressing the constitution of the substances they represent; but it is only in the case of the most simple compounds that this is strictly true; and, as regards the greater number of compound substances, chemical formulæ merely express the modes in which particular substances are capable of undergoing chemical alteration. Many substances are capable of chemical alteration in several different ways, and hence they may be represented by as many different formulæ. Thus, for instance, sulphuric acid may be represented by the formula H_2SO_4, which will serve to represent those alterations that correspond to the reaction between this substance and metallic zinc, consisting in the displacement of the hydrogen from sulphuric acid and the substitution of zinc in its place, forming a substance called zinc sulphate. In this case the displacement of the hydrogen takes place in accordance with the law of equivalents, and it is replaced by 32·5 times its weight of zinc. But in representing the change according to the atomic theory, it must be borne in mind that while hydrogen is a monovalent substance, zinc is bivalent. Consequently the two atomic proportions of hydrogen that are united with the bivalent radicle SO_4 in sulphuric acid are replaced by one atomic proportion of the bivalent metal zinc, and the formula of the zinc sulphate produced by this change is $ZnSO_4$.

Again sulphuric acid can be split up into water and sulphuric oxide, and this change is represented by the formula H_2O,SO_3 according to which sulphuric acid appears as a compound of water and sulphuric oxide.

Another decomposition of which sulphuric acid is capable is effected by the reaction with carbon, which gives rise to the formation of sulphurous oxide, SO_2, carbonic dioxide, CO_2, and water, H_2O; the change consisting in the abstraction of one-fourth of the oxygen from sulphuric acid by the carbon, with the consequent elimination of sulphurous oxide and water, and accordingly sulphuric acid may be represented by the formula SO_2OH_2O, as consisting of the radicle SO_2, combined with oxygen and water.

This illustration will serve to show that chemical formulæ, except in the case of such extremely simple compounds as hydrochloric acid, are to be regarded rather as a means of representing the possible changes that a substance may undergo than as an actual expression of their constitution, and this fact should always be borne in mind in making use of chemical formulæ, especially so in the case of substances of a complex nature.

A formula which merely indicates the relative atomic proportions of the elementary substances contained in the compound it represents is termed an **empirical** formula; but when it also indicates the constitution of the substance it is termed a **rational** formula.

In representing the constitution of compounds, it is frequently possible to regard a group of atoms as acting the part of an elementary substance. This is chiefly the case with complex compounds, and more especially those carbon compounds which are commonly called organic substances. Thus, for instance, alcohol which is represented by the empirical formula C_2H_6O may be regarded as the hydrate of such an atomic group or **radicle**, C_2H_5 performing in alcohol the same kind of function that one of the atomic proportions of hydrogen does in water; and ether, having the empirical formula $C_4H_{10}O$, may be represented as the oxide of the same radicle, and acetic acid as the hydrate of the oxygenated radicle C_2H_3O.

Another method of representing the constitution as well as the composition of substances is based upon the assumption that all compounds admit of classification in one or other of four groups, each comprising substances of analogous constitution or molecular type, the most simple instances of which are furnished by the substances hydrochloric acid, water, ammonia, and marsh gas. Substances of the most simple constitution, such as the chlorides, bromides, and iodides of monatomic elementary substances or radicles, are referrible to the hydrogen type, since their molecules may be regarded as consisting either of a pair of monovalent atoms, or of such an atom united with a monovalent radicle. Thus, for example, the molecules of hydrogen, of hydrochloric acid, and of ammonium chloride or ethyl chloride, are represented according to the hydrogen type by the formulæ:

	Hydrogen.	Hydrochloric acid.	Ammonium chloride.	Ethyl chloride.
AA	HH	HCl	NH_4Cl	C_2H_5Cl.

Another large class of substances are referrible to the water type, inasmuch as their molecules may be regarded as consisting either of a bivalent atom united with two monovalent atoms or radicles, or of a pair of bivalent atoms or radicles. So, for example, the molecules of water, caustic soda, and lime or alcohol, are represented by the typical formulæ:

	Water.	Caustic soda.	Lime.	Alcohol.
$\left.\begin{matrix}A\\A\end{matrix}\right\}A''$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}Na\\H\end{matrix}\right\}O$	CaO	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$

Substances which contain a trivalent atom or radicle are in like manner referrible to the ammonia type, as for example, the molecules of ammonia, ethylamine, phosphorus trichloride, and triethylamine:

	Ammonia.	Phosphorus trichloride.	Ethylamine.	Triethylamine.
$\left.\begin{matrix}A\\A\\A\end{matrix}\right\}A'''$	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right\}P$	$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N$

Lastly, the substances which contain a tetravalent atom or radicle are referred to the marsh gas type:

	Marsh gas.	Carbon tetrachloride.
$\left.\begin{matrix}A\\A\\A\\A\end{matrix}\right\}A^{iv}$	$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C$	$\left.\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right\}C$

The substances referrible to the water type are very numerous and varied, com-

prising many of the acids, salts, alcohols, ethers, etc. In these typical formulæ, compound radicles are represented as occupying the place of one or both of the hydrogen atoms in the molecule of water. Thus, for example, the acids are represented as being derived from water by the substitution of oxygenated radicles, as follows:

Nitric acid. $\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$ Acetic acid. $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$

The corresponding salts are represented as being derived from water by the substitution of an oxygenated radicle for one atom of hydrogen, and a monatomic elementary atom for the other, as follows:

Potassium nitrate. $\left.\begin{matrix}NO_2\\K\end{matrix}\right\}O$ Sodium acetate. $\left.\begin{matrix}C_2H_3O\\Na\end{matrix}\right\}O$

The composition of the several members of the alcohol and ether series can be represented by substituting for one or both hydrogen atoms in the water type one or two molecules of an alcohol radicle, as follows:

Ethylic alcohol. $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$ Amylic alcohol. $\left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\}O$ Ether. $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$ Amylic ether. $\left.\begin{matrix}C_5H_{11}\\C_5H_{11}\end{matrix}\right\}O$

The anhydrides may also be represented as being derived from water by the substitution of oxygenated radicles for both of the hydrogen atoms as follows:

Acetic anhydride. $\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$ Nitric anhydride. $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O$

A very considerable extension of the typical representation of substances is attained by means of multiple or mixed types. Thus, for instance, the duplication of the hydrogen type affords a means of expressing the composition of such substances as ethylene chloride, $C_2H_4Cl_2$, inasmuch as two hydrogen atoms in the typical formula $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}$ may be represented as replaced by the bivalent radicle ethylene, C_2H_4, and the other two by two monovalent atoms or radicles, or by a bivalent atom or radicle. Thus, for instance, by substitution of the bivalent radicle C_2H_4 for two hydrogen atoms in the double hydrogen type $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}$ it is possible to represent the composition of ethylene chloride and analogous compounds of bivalent elementary substances, as follows:

	Ethylene chloride.	Calcium chloride.	Calcium oxide.
$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}$	C_2H_4	Ca''	Ca''
	Cl_2	Cl_2	O

By multiplying the water type in the same manner the composition of many other substances may be represented, for example, the compounds of bivalent elementary substances and radicles, such as the polybasic acids, etc., by substituting for two or more atoms of the typical hydrogen in these formulæ acid radicles or metals, as follows:

	Sulphuric acid.	Calcium hydrate.	Oxalic acid.	Glycol.		Phosphoric acid.
$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}Ca''\\H^2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}PO'''\\H_3\end{matrix}\right\}O_3$

The formulæ of the corresponding salts are obtained by substituting for the rest of the hydrogen equivalent quantities of the metals:

	Zinc sulphate.	Sodium sulphate	Sodium phosphate.
$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}SO_2\\Zn\end{matrix}\right\}O_2$	$\left.\begin{matrix}SO_2''\\Na_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}PO'''\\Na_3\end{matrix}\right\}O_3$

Acid salts are similarly represented as follows:

Acid sodium sulphate. $\left.\begin{matrix}SO_2\\HNa\end{matrix}\right\}O_2$ Acid sodium phosphates. $\left.\begin{matrix}PO\\HNa_2\end{matrix}\right\}O_3$ $\left.\begin{matrix}PO\\H_2Na\end{matrix}\right\}O_3$

INORGANIC CHEMISTRY.

SUBSTANCES OCCURRING AS MINERALS.

The separate consideration of the general chemical relations of the elementary substances, and of those compounds of them which either occur among the materials constituting the mass of the earth, or can be produced from these latter by making them act upon each other under the influence of heat or other conditions, has long been found convenient, because the facts to be dealt with are for the most part of a more simple character than those relating to the chemistry of the materials of which plants and animals consist. Hence the distinction that is made between inorganic chemistry and organic chemistry is one justified to some extent by the nature of the subject matter appertaining to each section of the science. But at the same time it must be remembered that this distinction is otherwise merely an artificial one. There is no longer any reason, even of a theoretical kind, for retaining the opinion formerly entertained that the chemical phenomena presented by the organised structure of plants or animals are in any way essentially different from those presented by mineral substances. Both classes of phenomena are subject to the same general laws, and, although the individual substances produced by plants and animals, or artificially derived from their products, are as a class characterised by a peculiarity of composition, inasmuch as they all consist of only a small number of the elementary substance, and always contain carbon as a prominent constituent, they differ from mineral or inorganic substances only in the same manner that certain classes of these latter substances, as, for example, the compounds of iron or the compounds of copper, differ from other classes of inorganic substances.

Moreover, there is in many instances considerable difficulty in deciding whether certain substances should be included amongst inorganic or organic compounds, and one of the most important results of modern progress in chemical science has been the discovery of methods by which a large number of substances, ordinarily produced by plants or animals, can be obtained by the direct or indirect combination of their elementary constituents.

Consequently the separation of the subjects treated of in the subsequent pages, under the two heads of inorganic chemistry and organic chemistry, is to be regarded as a purely arbitrary device, having for its object merely the convenience of treating of the general chemical relations of all the elementary substances and their compounds, under the first head, while the consideration of the carbon compounds derived from plants and animals is specially dealt with under the second head.

Among the substances which are properly classed as inorganic, there are many which occur naturally as minerals in a state which cannot be reproduced by artificial means. Thus, for instance, some of the metallic compounds constituting ores are often found in the form of crystals, and presenting physical characters widely different from those of the same substances prepared by the combination of elementary substances. This circumstance is referrible to the difference in the conditions under which such substances have been formed. The crystallised metallic compounds occurring in ores, and the various crystallised minerals occurring as constituents of different rocks, such as granite, hornblende schist, micaceous schist, etc., are most probably the products of very gradual and long-continued chemical action, and perhaps also their formation has been the result of other determining conditions which it is impossible to imitate. In like manner the physical condition of extensive masses of rocks such as marble, granular limestone, slate, sandstone, etc., is the result of long-continued chemical action.

The several rocks comprised under the general term of metamorphic rocks have always furnished wide scope for speculation as to the mode in which they have acquire

their present condition. These rocks, presenting evident signs of stratification, fossil-remains and, sometimes, all the features of sedimentary strata, also possess a crystalline structure, and sometimes resemble massive crystalline rocks so closely as to be distinguishable from them only by retaining faint signs of stratification which reveal their sedimentary origin. Hence it is impossible to regard the present condition of these rocks otherwise than as having been brought about by the chemical no less than the physical alteration of sedimentary strata. Similar evidence of chemical alteration is afforded by crystalline minerals which almost always contain substances not belonging to their chemical constitution,

In seeking to arrive at a knowledge of the means by which such gradually progressive alterations of minerals and rocks are effected, it is necessary to take into account a variety of influences which, though infinitesimal in themselves within ordinary periods of observation, are nevertheless capable of producing, by long continuance, effects which appear, at first sight, disproportionate. Chief among these are the actions exercised by water as a solvent, and by the substances it holds in solution when brought into contact with rocks or minerals. The uniformity in the characters of the water of mineral springs shows that processes of chemical alteration are continuous and of considerable magnitude at great depths below the earth's surface, while the occurrence of large masses of minerals such as kaolin, evidently originating from felspathic rocks by the abstraction of some of their constituents, indicates that they are the result of similar slow chemical action.

The masses of metallic compounds occurring in the form of veins extending through the older rocks, and known by the name of lodes, are especially interesting in this respect, as they offer a striking illustration of the way in which chemical action in past conditions of the earth's existence has been operative in effecting a concentration of the materials from which industrial art now derives some of its most important products.

In regard to other geological phenomena in which the effect of chemical action can be more distinctly traced it soon becomes apparent, in considering them from a chemical point of view, that there are two forms in which chemical action has influenced the successive changes which it is the province of geology to study, and of which the superficial strata of the earth furnish the evidence and record. At the present time chemical action is abundantly exerted in various ways, in effecting the alteration of existing materials, and there are likewise some instances where it may be observed as producing a constructive effect; but in this latter aspect, chemical action is far more rarely susceptible of direct observation as an element of geological phenomena than it is in its destructive phase. For the most part, the constructive influence of chemical action in regard to geological phenomena can be observed only indirectly, and the evidence of its exercise is much of the same nature as that which serves to determine the relative age of the earth's strata, the climatic or other conditions prevailing at the time of their formation as well as their marine or freshwater origin.

OXYGEN.

Symbol O. Atomic Weight 16.

History.—This substance was discovered in 1774 by Priestley in England, and also about the same time by Scheele in Sweden. These chemists studied some of the most important properties of the gas, which was at last called *dephlogisticated* or *vital* air. Lavoisier was, however, the most active and successful in this respect, since he made the important discovery that the combustion of substances in atmospheric air consists in their chemical combination with oxygen. This discovery of Lavoisier's was one of great moment for the development of chemical science, since it served to overthrow the fundamental hypothesis of the phlogistic theory, according to which the substance burnt in any such case of combustion was supposed to be converted into 'Calx' and 'Phlogiston.' From this discovery of oxygen, and the knowledge of its most essential properties, dates the modern era of chemical science.

Occurrence.—Oxygen is a very abundant substance, constituting about one-third of the known terraqueous globe. In the free or uncombined state it constitutes nearly one-fifth part by weight of atmospheric air. Oxygen occurs in still greater quantity chemically combined with other substances, as in water, eight-ninths by weight of which is oxygen, in almost all minerals and rocks, and in most organic substances.

Characters.—Oxygen in the uncombined state is a colourless and odourless gas that has hitherto resisted all attempts to render it liquid or solid by means of pressure and cold. It is slightly denser than atmospheric air, having a specific gravity of 1·1056 (air = 1); and, relatively to hydrogen = 1, the density of oxygen is 16. Its power of refracting light is less than that of any other gas.

Oxygen is sparingly soluble in water, which at the ordinary temperature dissolves about 3 per cent. of its volume.

Oxygen possesses considerable chemical activity, and it is capable of combining directly with a great number of elementary and compound substances. The chemical change thus produced is termed *oxidation*. This character of oxygen is manifested in a variety of ways by the oxygen existing in the atmosphere, although there it exists largely diluted with another gas; hence many of the changes that substances undergo when in contact with atmospheric air are due to oxidation. The rusting of iron is a familiar instance of change resulting from combination with atmospheric oxygen, and a number of other phenomena are essentially though less obviously of a similar nature.

Under the influence of the electric current, oxygen gas is converted into an allotropic condition, in which it possesses other special properties, and acts far more energetically as an oxidising agent.

Preparation.—Several metallic oxides, such as auric oxide, argentic oxide, mercuric oxide, disengage their oxygen when merely heated to a temperature ranging from 100° to 150° C. Consequently it is very easy to prepare oxygen by heating some one of these oxides in a close vessel furnished with a bent delivery-tube terminating under a bell glass filled with water and immersed with its mouth downwards in a vessel of water.

Mercuric oxide, when heated in a glass tube, is decomposed into metallic mercury and oxygen in the following proportions:—

HgO	=	Hg	+	O
216		200		16

And for preparing small quantities of oxygen it is a very convenient material.

But the high price of such metallic oxides would render the preparation of oxygen from them on a large scale very costly, for with the greatest care in manipulation a loss of some portion of the substance employed is not to be avoided.

A more economical method of preparing oxygen consists in decomposing the peroxide of manganese, which occurs abundantly in Spain, England, Germany, and France as a mineral, and is known as manganese-ore.

When manganese peroxide is heated to redness, it gives up a portion of its

oxygen, and a compound of manganic and manganous oxides remains. This change is represented by the following equation:

$$\begin{array}{ccccc} 3MnO_2 & = & Mn_3O_4 & + & 2O. \\ 261 & & 229 & & 32. \end{array}$$

According to this, manganese peroxide will yield one-third of its oxygen, and as it contains 36·78 per cent. by weight of oxygen, the yield from manganese-ore, when pure, will amount to 12·26 per cent.

The apparatus employed for this purpose is represented in section by fig. 1; it consists of a wrought-iron cylindrical vessel (A) with a narrow neck, into which is fitted one end of an iron delivery-tube (B), while the other end is connected by means of a cork (C) with a bent glass tube dipping under the shelf of a pneumatic trough (E E) filled with water.

The iron cylinder (A), partly filled with manganese-ore, is heated in the furnace (G G G)

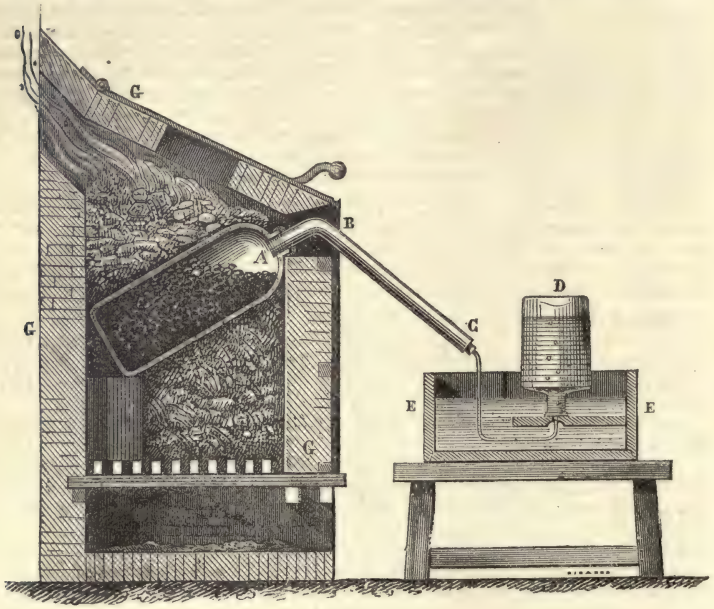


FIG. 1.

until the decomposition of the peroxide commences and bubbles of gas escape through the water in the pneumatic trough from the end of the glass tube. A bottle (D), completely filled with water, is then inverted over the end of the tube so as to collect the gas.

The first portion of gas given off carries with it the air contained in the apparatus, so that if pure oxygen be required, it is necessary to wait until all the air has been driven out before beginning to collect the gas.

It is possible to obtain from manganese ore one-half of the oxygen it contains, or 18·39 per cent. by weight instead of 12·26, by carefully treating a mixture of the powdered mineral with an excess of sulphuric acid. The reaction in this case is represented by the following equation:

$$\begin{array}{ccccccccc} MnO_2 & + & H_2SO_4 & = & MnSO_4 & + & H_2O & + & O \\ 87 & & 98 & & 151 & & 18 & & 16 \end{array}$$

As the temperature at which sulphuric acid acts upon manganese peroxide with evolution of oxygen is not very high, this operation can be safely conducted in a glass flask (A, fig. 2) heated over a gas flame, the bottom of the flask being protected by a piece of wire gauze.

Since commercial manganese ore often contains carbonates, and carbonic acid is sometimes liberated even when the mineral is treated alone or more certainly when it is treated with sulphuric acid, the gas obtained from this source is often impure. For

its purification it is passed through a Woulfe's bottle (B) half filled with a strong solution of soda or potash. In this way all the carbonic acid is absorbed, and the oxygen passing out through the delivery tube of B can be collected either in an inverted glass cylinder (C) over a pneumatic trough, or in a gasholder.

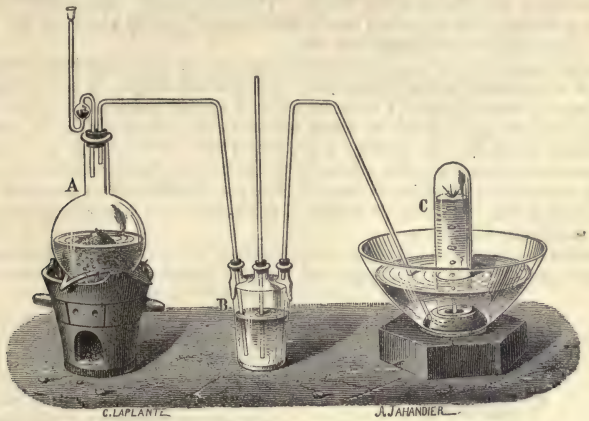


FIG. 2.

Potassium chlorate is a convenient source of oxygen, inasmuch as it is decomposed by heating and, giving up the whole of its oxygen, is converted into potassium chloride according to the following equation:—

$$\underset{122{\cdot}5}{KClO_3} = \underset{74{\cdot}5}{KCl} + \underset{48}{3O}$$

This salt is therefore capable of yielding 39·16 per cent. by weight of oxygen, and, when all the gas has been expelled by heat, 60·84 per cent. of potassium chloride, which remains in the generating apparatus as a solid mass easily soluble in water.

This decomposition really takes place in two stages, the first resulting in the conversion of part of the chlorate into perchlorate as follows:—

$$\underset{245}{2KClO_3} = \underset{74{\cdot}5}{KCl} + \underset{138{\cdot}5}{KClO_4} + \underset{32}{2O}$$

and then, by the application of a more intense heat, the perchlorate gives up all its oxygen, potassium chloride remaining:—

$$\underset{138{\cdot}5}{KClO_4} = \underset{74{\cdot}5}{KCl} + \underset{64}{4O}$$

In this latter stage of the process the decomposition is so sudden that the melted potassium chloride is liable to froth over, and the heat requisite is so great that glass flasks often soften and give way.

Potassium chlorate decomposes, however, at a comparatively low temperature, when mixed with manganese peroxide, while the manganese peroxide remains unaltered, acting simply as a diluting material, and mechanically by the surface it presents.

In order to obtain a constant and strong development of oxygen, it is better to make use of a mixture of equal parts of powdered manganese ore and potassium chlorate. The apparatus represented by fig. 2 serves for this purpose.

During the last few years attempts have been made to isolate the oxygen from atmospheric air, where it exists in such large quantity. One of the most practicable methods for this purpose consists in heating moist cuprous chloride, with access of air, to a temperature ranging from 100° to 200° C., in a rotatory cast-iron retort, the interior of which is protected against the action of the charge or of the products developed from it by a suitable coating. Under these conditions oxygen is absorbed from the air, cuprous oxychloride being formed; and when this is heated to 400° C., it gives up again the oxygen it had absorbed from the air. In carrying out this process, it is of practical advantage to mix the cuprous chloride with sand or powdered kaolin, in order to prevent it from melting. In this way cuprous chloride mixed with sand yields, for each 100 kilograms, from 3 to 3½ cubic metres of oxygen; and as the operation can be repeated four or five times daily, it is possible to produce in

this space of time from 15 to 18 cubic metres of oxygen from 100 kilograms of cuprous chloride. Other methods of isolating oxygen from the atmospheric air, as, for instance, by means of peroxide of barium, do not appear to be practically advantageous.

Collection and Storage of Gases.—The glass vessels represented in figs. 1 and 2 are only suitable for collecting small quantities of gas by means of the pneumatic trough, when required for immediate use.

If larger quantities of gas are required than can be conveniently collected in glass vessels, it is necessary to use a gasholder made of sheet copper, as represented by fig. 3, consisting of a close cylinder (A B) furnished with a glass gauge (*h h*), and at the bottom with a lateral neck (*g*) that can be closed with a screw plug or a cork. A smaller cylindrical vessel (C D), open at the top, is supported upon three pillars above A B. These cylinders are connected together internally by the tubes (*e f*), both furnished with taps so that the communication between the cylinders may be shut off at pleasure. The tube *f* extends from the bottom of C D nearly to the bottom of A B, while the tube *e* is immediately inside the top of A B.

In order to prepare the gasholder for collecting a gas, the neck (*g*) is closed and both the taps *e* and *f* opened. Water poured into the upper cylinder will then flow down the tube *f*, while the air in A B escapes through the tube *e*. When the cylinder (A B) is quite filled with water, the taps are closed and the lateral neck (*g*) is opened so as to allow the delivery-tube from the gas-generating apparatus to be inserted. The gas streaming into A B will then displace the water, and force it out through the neck (*g*) into the pan (*j j*). As soon as A B is filled with gas, which may be ascertained by the water-level in the glass gauge (*h h*), the gas delivery-tube is removed and the neck (*g*) closed.

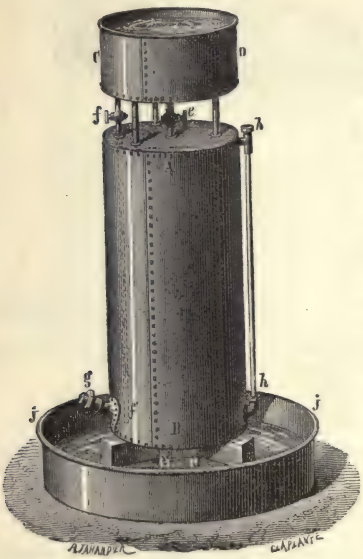


Fig. 3.

In using the gasholder thus charged with a gas, the cylinder (C D) is filled with water and the tap in the tube (*f*) opened so as to allow water to flow into A B and compress the gas it contains. Then, on opening the tap in the tube *e*, the gas will escape as water flows in through *f*, and it may be collected in a glass jar filled with water and inverted over the mouth of the tube *e*. Sometimes it is convenient to have a lateral tube with a tap attached to the side of A B at the top, so as to obtain a continuous stream of gas.

Uses.—In confined spaces, where the air cannot be replaced, it has been attempted with good success to make use of oxygen in order to maintain the air in a respirable condition. Many such experiments have been made, with diving-bells more especially. Oxygen is also much used in chemical laboratories, chiefly for oxidising various substances in chemical analysis. In a subsequent chapter it will be explained how oxygen is used in combination with hydrogen for obtaining high temperatures.

Without doubt, oxygen gas would be very much used for the production of light and heat, for the oxidation of sulphur, and for the roasting of certain ores, etc., if it could be more cheaply prepared. But up to the present time, notwithstanding many attempts in this direction, there is still no method of preparation known which would admit of the general use of oxygen for such purposes.

Compounds.—With the probable exception of fluorine, all the elementary substances form compounds with oxygen, which are termed oxides. Many of these substances occur naturally in great abundance, and some of them are of great importance as the sources of various metals. Others are prepared artificially, and extensively used for a variety of purposes.

Oxides are classified according to the atomic proportions of oxygen they contain, as monoxides, dioxides, trioxides, tetroxides, pentoxides, etc., the prefix in each case indicating the number of oxygen atoms in the molecule. When a substance

combines with oxygen in more than one proportion, the oxide containing the least oxygen is often called protoxide and one of those containing more oxygen is sometimes called peroxide. Several of the trioxides are also termed sesquioxides when they contain half as much oxygen again as the corresponding protoxides. Oxides containing different proportions of oxygen are often distinguished by adding to the name of the substance they contain in common, the terminations ous and ic; for example, sulphurous oxide and sulphuric oxide, ferrous oxide and ferric oxide, cuprous oxide and cupric oxide.

The formulæ in the accompanying table represent the composition of the more important oxides of the elementary substances.

	Monoxides		Dioxides		Trioxides		Tetroxides		Pentoxides	
Carbon	—	CO	—	CO_2	—	—	—	—	—	—
Silicon	—	—	—	SiO_2	—	—	—	—	—	—
Titanium	—	—	—	TiO_2	—	—	—	—	—	—
Sulphur	—	—	—	SO_2	—	SO_3	—	—	—	—
Selenium	—	—	—	SeO_2	—	SeO_3	—	—	—	—
Tellurium	—	—	—	TeO_2	—	TeO_3	—	—	—	—
Molybdenum	—	—	—	MoO_2	—	MoO_3	—	—	—	—
Tungsten	—	—	—	—	—	WO_3	—	—	—	—
Boron	—	—	—	—	B_2O_3	—	—	—	—	—
Chlorine	Cl_2O	—	—	ClO_2	Cl_2O_3	—	—	—	—	—
Iodine	—	—	—	—	—	—	—	—	—	I_2O_5
Nitrogen	N_2O	NO	—	NO_2	N_2O_3	—	—	—	—	N_2O_5
Phosphorus	—	—	—	—	P_2O_3	—	—	—	—	P_2O_5
Arsenic	—	—	—	—	As_2O_3	—	—	—	—	As_2O_5
Antimony	—	—	—	—	Sb_2O_3	—	Sb_2O_4	—	—	Sb_2O_5
Bismuth	—	—	—	—	Bi_2O_3	—	—	—	—	Bi_2O_5
Gold	Au_2O	—	—	—	Au_2O_3	—	—	—	—	—
Tin	—	SnO	—	SnO_2	Sn_2O_3	—	—	—	—	—
Platinum	—	PtO	—	PtO_2	—	—	—	—	—	—
Palladium	—	PdO	—	PdO_2	—	—	—	—	—	—
Aluminium	—	—	—	—	Al_2O_3	—	—	—	—	—
Uranium	—	UO	—	—	U_2O_3	—	—	U_3O_4	U_4O_5	—
Cobalt	—	CoO	—	—	Co_2O_3	—	—	Co_3O_4	—	—
Nickel	—	NiO	—	—	Ni_2O_3	—	—	Ni_3O_4	—	—
Iron	—	FeO	—	—	Fe_2O_3	—	—	Fe_3O_4	—	—
Manganese	—	MnO	—	MnO_2	Mn_2O_3	—	—	Mn_3O_4	—	—
Chromium	—	CrO	—	CrO_2	Cr_2O_3	CrO_3	—	Cr_3O_4	—	—
Lead	Pb_2O	PbO	—	PbO_2	—	—	—	Pb_3O_4	—	—
Mercury	Hg_2O	HgO	—	—	—	—	—	—	—	—
Copper	Cu_2O	CuO	—	—	—	—	—	—	—	—
Silver	Ag_2O	—	Ag_2O_2	—	—	—	—	—	—	—
Barium	BaO	—	BaO_2	—	—	—	—	—	—	—
Strontium	SrO	—	SrO_2	—	—	—	—	—	—	—
Calcium	CaO	—	CaO_2	—	—	—	—	—	—	—
Potassium	K_2O	—	K_2O_2	—	—	—	—	—	—	—
Sodium	Na_2O	—	Na_2O_2	—	—	—	—	—	—	—
Hydrogen	H_2O	—	H_2O_2	—	—	—	—	—	—	—

With the exception of water, and some oxides of the metalloids which are gaseous under ordinary conditions of temperature, most of the oxides of elementary substances are solid. Many of them melt at various degrees of heat, and a few are volatilisable; some are readily and entirely decomposed by heating, others are merely converted into lower oxides with partial evolution of oxygen; and several of them are not in any way altered by the highest temperatures that can be produced.

Many of the oxides are capable of combining with each other and form compounds termed salts, in which the characters of the constituents are masked or neutralised, and those oxides which are most dissimilar in themselves or in the characters of the elementary substances they contain are most susceptible of such combination. Thus, for instance, nitric pentoxide or sulphur trioxide combines with metallic oxides, forming two series of saline compounds called nitrates and sulphates, the compounds with sodium monoxide being cubic nitre, or sodium nitrate, and sodium sulphate, or the substance known as Glauber's salt.

$$N_2O_5 + Na_2O = 2NaNO_3 \text{ and } SO_3 + Na_2O = Na_2SO_4$$

The oxides which, like iodic, nitric, phosphoric, boracic, arsenic oxides, etc., correspond with sulphuric oxide in this respect are called acid oxides, and they form several series of salts called iodates, nitrates, phosphates, borates, arsenates, etc. The oxides corresponding with sodium monoxide are called basic oxides. This distinction between oxides on the ground of their chemical relations is, to a certain extent, consistent with the distinction between elementary substances as metals and metalloids, inasmuch as the acid oxides are chiefly oxides of metalloids, while the oxides of the metals are chiefly basic oxides.

The acid or basic character of an oxide seems, however, to be in some cases as much determined by the proportion of oxygen it contains as by the nature of its other elementary constituents, since several of the lower oxides of metals are basic oxides and the corresponding higher oxides are acid oxides. Thus, for instance, chromous oxide (CrO) is a decidedly basic oxide, while the trioxide (CrO_3) is as decidedly an acid oxide.

The capability of assuming in this respect opposite chemical relations is especially marked in the case of hydrogen monoxide, or water, which combines with acid oxides, as well as basic oxides, forming compounds which differ in some respects from the generality of salts. Thus, for instance, sulphuric oxide combines with water, forming a compound corresponding to sodium sulphate $SO_3 + H_2O = H_2SO_4$ or hydrogen sulphate, in which the acid character of the oxide is rather intensified than neutralised as in other sulphates. This is the case with all the acid oxides, and hence the corresponding hydrogen salts are specially designated **acids**; hydrogen sulphate, for instance, being ordinary sulphuric acid and hydrogen nitrate HNO_3 nitric acid.

In the compounds of basic oxides with water likewise the basic characters of those oxides are not neutralised as in ordinary salts, but are even more marked than in the oxides themselves, as in the case of the compounds of calcium oxide, or quicklime, and sodium monoxide with water $CaO + H_2O = H_2CaO_2$ and $Na_2O + H_2O = 2HNaO$. On this account the compounds of basic oxides with water are often termed **hydrated oxides** or **hydrates**, as calcic hydrate, sodium hydrate, or sometimes **bases**, to distinguish them from salts generally, and from acids or the hydrogen salts of acid oxides. The distinction, however, is merely conventional, since the compounds of acid oxides with water might equally be termed hydrates of those oxides, *e.g.* sulphuric hydrate, nitric hydrate, etc.

Combustion.—The direct combination of oxygen with other substances is always attended with considerable evolution of heat, and in many natural operations some process of oxidation is the principal source of heat. It is also the only means by which heat is produced artificially. In many instances when oxidation takes place rapidly it gives rise to the phenomenon of combustion, the temperature of the substance produced by the combination being raised to such a degree by the heat evolved as to render it luminous, as in the burning of fuel or of the materials used for obtaining light. These effects are also produced by some other kinds of chemical action, but they are so much more frequently the result of oxidation that the term **combustion** is specially applied to the evolution of heat and light attending oxidation. In all ordinary cases of combustion the burning substance combines with oxygen derived from the atmospheric air immediately surrounding it; sulphur in burning being oxidised to sulphurous oxide, phosphorus to phosphoric oxide, carbon to carbonic dioxide, and hydrogen to hydric oxide or water. Oxygen is therefore termed a **supporter of combustion**, and substances that are capable of combining with oxygen in this way are termed combustible substances.

The combination of oxygen with substances in this way does not take place at the ordinary temperature except in a few very rare instances; and in order to make any substance burn it must be heated to the particular temperature or **burning-point** at which it enters into combination with oxygen, or in ordinary language *takes fire*. When this combination has once commenced it is generally maintained by the heat always evolved in the process, so long at least as there is an available supply of oxygen and any of the combustible substance remains unburnt.

A number of substances that do not burn readily or at all in atmospheric air can be burnt in pure oxygen. Iron-wire, for instance, burns with brilliant coruscations when made red-hot at the end and introduced into pure oxygen gas. Carbon, sulphur, phosphorus, and other combustible substances, also burn in oxygen with much greater luminous intensity than in atmospheric air. Phosphorus especially burns with such a dazzling light that the eye cannot bear it. The fact admits of oxygen being easily recognised. If, for instance, an incandescent wood splinter be inserted into a vessel containing oxygen it immediately begins to burn with an intensely bright light. Nitrous oxide is the only other gas that produces a similar effect, and that can be distinguished from oxygen by its greater solubility in water, and by not forming red fumes with nitric oxide gas as oxygen does.

The particular phenomena presented by substances in burning depend to a great extent upon the physical condition of the combustible substances themselves and of the products of their oxidation. Thus, for instance, substances that are gaseous burn with flame, and this is also the case with solids or liquids that are capable of assuming the state either of gas or vapour. Substances that do not assume the gaseous condition in burning give no flame. In both cases combination with oxygen takes place when the burning substance is in contact with atmospheric air; and while a non-volatilisable substance, such as charcoal or iron, burns without any considerable alteration in the bulk of the unoxidised mass, the phenomenon of flame presented in the combustion of a gas or vapour is simply a result of the mobility and expansibility belonging to substances in that physical condition. Flame is, in fact, merely intensely heated gas.

When oxidisable gases are mixed with a sufficient proportion of oxygen gas or atmospheric air for their oxidation and brought into contact with flame, combination takes place suddenly through the entire mass, and the expansion of the gas by the heat evolved causes a violent concussion. Combination taking place in this way is termed explosion.

The quantity of heat evolved in oxidation differs according to the nature of the substance oxidised, and according to the proportion of oxygen with which the substance combines. Thus hydrogen evolves considerably more heat when burnt than an equal weight of carbon does, and when carbon is burnt to carbonic dioxide the quantity of heat evolved is much greater than when it is burnt to carbonic oxide.

The following table gives the quantities as well as the relative amounts of heat evolved in the direct oxidation of several elementary substances:—

	Product of oxidation	Quantity of heat generated	Relative heat of oxidation
		Heat-units	
Hydrogen	H_2O	33881	4·23
Carbon	CO_2	8000	1·
Sulphur	SO_2	2307	0·29
Phosphorus	P_2O_5	5747	0·72
Iron	Fe_2O	1582	0·19
Zinc	ZnO	1330	0·17
Tin	SnO_2	1147	0·14
Copper	CuO	603	0·07

According to these data the actual quantity of heat evolved in the oxidation of 1 gram of carbon to carbonic dioxide is sufficient to raise the temperature of 8,000 grams of water one degree, or of 80 grams from 0° to 100°. The heat generated in the oxidation of hydrogen is more than four times as much.

The immediate effect of the heat evolved in combustion is to raise the temperature of the substance produced, and then the heat is gradually dispersed by conduction throughout the mass of contiguous substances as well as by radiation. The increase of temperature thus produced is to a great extent dependent upon and proportionate to the rate of oxidation, and the higher degrees are distinguished according to the colour of the light emitted by the heated substance, as red heat, white heat, etc. In every case, however, there is a limit to the temperature that a substance can produce by its combustion. The conditions that influence this will be treated of under the head of 'Fuel.'

The light emitted in combustion depends very much upon the temperature produced; but it is also considerably influenced by the physical condition of the combustible substance and that of the product of oxidation, as well as by the temperature to which it is heated. Solids such as carbon or iron, that burn without vapouring, are capable of emitting a very intense light in combustion. The flame of hydrogen, however, is but very feebly luminous, although its temperature is much higher than that produced by the combustion of iron or of carbon. The luminous intensity of flame is also greater in proportion to the density of the vapour or gas burnt and of the gaseous products formed; paraffin, for instance, burns with a very luminous flame, while marsh gas, a substance of the same chemical composition, burns with only a faint light, the density of this gas being very considerably less than that of paraffin vapour. The presence of solid particles in a flame, as a result either of the change produced by oxidation or of other conditions, is another circumstance that considerably augments the luminous intensity, especially if the temperature be high. Thus zinc and phosphorus, both furnishing solid products by oxidation, give intensely luminous flames when burnt. The light emitted by the flame of a candle or of coal gas is probably due in

some degree to the presence of solid particles of carbon originating from the decomposition of carbonaceous vapours.

Since free oxygen is everywhere present as a constituent of the atmosphere upon the earth's surface, a great number of processes of oxidation are continually going on; but in many cases the oxidation takes place so slowly that no development of heat or light can be perceived. Thus several metallic sulphides, when exposed to the air, are gradually oxidised to sulphates; many organic substances absorb oxygen from the air, and by combining with it produce other compounds. This last kind of oxidation is called slow combustion, in opposition to that rapid combustion which is accompanied by the obvious development of light and heat. The actual amount of heat evolved is, however, the same, whether the oxidation of a substance takes place slowly or rapidly, the only difference being in the intensity of the effect produced.

Many substances which oxidise but slowly when in compact masses are much more readily oxidised when they are in a state of minute subdivision and there is relatively to the mass a very much larger surface exposed to contact with atmospheric air. Thus, for instance, when the finely divided metallic iron obtained by the action of hydrogen upon powdered ferric oxide at a red heat is brought into contact with atmospheric air, it is suddenly oxidised with evolution of heat and light. In such cases oxidation may also be promoted to some extent by the capability which most porous substances possess of absorbing and condensing gases. The spontaneous combustion of greasy rags, cotton, tow, etc., when heaped up in a confined space, is due to the accelerated oxidation of the fatty substance with which these porous materials are impregnated, and the consequent heating of the mass to a temperature at which rapid combustion takes place.

The process of animal respiration, regarded from a chemical point of view, is a case of slow combustion. Animals, by the operation of breathing, supply their bodies continually with oxygen from the air; the oxygen thus inhaled combines with the carbon and hydrogen of organic substances, and is again exhaled as carbonic acid and water-vapour. This process serves especially to illustrate the fact that in slow combustion heat is liberated, for it is by this means that the supply of heat necessary for the life of animals is generated. The liberation of heat, however, takes place very slowly, and therefore it is not so easily recognisable as in cases of rapid combustion.

OZONE.

History.—The fact that a peculiar alliaceous odour is sometimes communicated to atmospheric air by a flash of lightning or other forms of electrical discharge, has long been known and frequently observed in various ways. In 1785 Van Marum found that it was the oxygen of the atmosphere which acquired this odour. In 1840 Schönbein specially investigated this subject, and having ascertained that the peculiar smell observed in the proximity of the electrical machine, and other electrical apparatus, was due to the presence of a peculiar gas, which is also formed when water is decomposed by electrolysis, he gave the name of ozone to the substance possessing this character. It is only recently, however, that the researches of Andrews, Soret, and others have shown that ozone is an allotropic form of oxygen.

Occurrence.—Ozone occurs in the atmosphere in varying proportions, according to locality and season, and it is probably produced chiefly by the action of atmospheric electricity. In country places it is most abundant, but does not amount to more than $\frac{1}{450000}$th part by weight, or $\frac{1}{700000}$th part by volume of atmospheric air. The amount is greatest in spring and least in winter.

Characters.—Ozone is very different in its characters from ordinary oxygen. It possesses a penetrating smell, acts violently upon the organs of respiration like chlorine, and is the most energetic oxidising agent that is known. While oxygen at the ordinary temperature acts directly upon only a few substances, almost all oxidisable substances are oxidised upon being brought into contact with ozone. The density of ozone appears to be 1·5 times that of oxygen: it is less soluble than oxygen in water, which dissolves only about 0·5 per cent. of its volume. Ozone, placed in contact with potassium iodide, sets the iodine free. Upon this reaction depends a delicate means of ascertaining the presence of ozone. If air or a liquid containing ozone be brought into contact with a dilute aqueous solution of potassium iodide, to which a small quantity of starch paste has been added, the liquid is coloured blue by the liberated iodine combining with the starch. When air has to be tested for ozone, it is more convenient to make use of a strip of bibulous paper which has been saturated with a solution of starch containing potassium iodide. But since iodine is similarly liberated from potassium iodide by chlorine, by some nitrogen oxides, and other substances, this test cannot be relied upon implicitly.

The instruments termed ozonometers consist essentially of strips of paper prepared in the way above mentioned: when brought into air containing ozone, they would indicate the amount of ozone contained in the air by the degree of intensity of the blue coloration produced. Since the actual quantity of ozone corresponding to a particular degree of blue coloration is not known, such ozonometers only indicate the relative amounts of ozone in the air. The possible presence of nitrogen oxides in atmospheric air renders the indications of these instruments very uncertain. A better test consists of red litmus paper, with half its surface impregnated with a one per cent. solution of potassium iodide. The portion of the paper thus impregnated becomes blue by contact with air containing ozone, in consequence of oxidation and the formation of potash. The unimpregnated portion of the paper is not at all altered unless the air contains ammoniacal vapours, and then the paper becomes blue over its entire surface.

Ozone exerts an oxidising action upon many organic substances, destroying some entirely, oxidising others only to a certain extent. Thus, for instance, ozone destroys the colour of many plants, bleaching them entirely; but tincture of guaiacum is only rendered blue by this agent.

If ozone be conducted through a glass tube heated to redness, it is decomposed, the volume of the gas is permanently increased, and ordinary oxygen is formed. Ozone is also converted into ordinary oxygen at a temperature of 250° to 300°.

Ozone acts in a very remarkable manner upon certain peroxides. When brought into contact with barium peroxide, hydrogen peroxide, or other peroxides, it is converted into ordinary oxygen, while the peroxides also give up a part of their oxygen and are converted into lower oxides.

Preparation.—Though ozone is always present in small quantity in the atmosphere, still it cannot be obtained from that source in such a concentrated condition that all its characteristic properties are evident. It is not, in fact, possible to prepare pure ozone, and what is called ozone is only air or oxygen containing some admixture of ozone.

Ozone is produced in every case where electrical discharges take place in the air, as in the production of sparks by electrical machines, etc. During a thunderstorm also a strong odour of ozone is often noticeable. Ozone is formed, moreover, in considerable amount when phosphorus, partially immersed in water, is exposed to the air, and when dry potassium permanganate is decomposed with strong sulphuric acid, also in the combustion of hydrogen in the air.

Lastly, there are many substances called ozone bearers, which exhibit the ozone reaction with potassium iodide, and are therefore supposed to become ozonised upon prolonged contact with the air. To this class of bodies belong especially a number of ethereal oils, oil of turpentine, oil of citron, etc. It is, however, probable that the reaction these oils produce, after exposure to the air, is due to compounds of the oils with oxygen.

Uses.—Ozone has often been proposed as a bleaching agent, for decolorising stearin, wax, and other organic substances, which either cannot stand the process of bleaching with sulphurous acid and chlorine, or are not sufficiently bleached by these substances. However, bleaching with ozonised air has not at present supplanted the natural bleaching of those organic materials. Ozone has also been proposed for disinfection; and it would no doubt prove very suitable for this purpose if it could be more easily and cheaply obtained, for on account of its energetic action upon most organic substances, it is to be presumed that it would destroy the organic miasma of bad air. Whether ozone might be employed as a preservative against cholera, and whether any connection exists between the ozonic contents of the air and the appearance of that disease, is at present uncertain.

HYDROGEN.

Symbol H. Atomic Weight 1.

History.—The statements of the older chemists as to the properties of hydrogen are very vague, and partly inexact, since the inflammable gas produced by dissolving metals in dilute acids was confounded with other inflammable gases of a different nature, such as marsh gas, etc. Cavendish was the first who made exact experiments with this gas. It was at first named inflammable air; afterwards the antiphlogistic chemists gave it the name hydrogen—from ὕδωρ water, and γεννάω to generate—for the purpose of indicating that, by its combination with oxygen, it produces water.

Occurrence.—Hydrogen seldom occurs naturally in the free state, and only in very small quantities, as in volcanic exhalations. It has also been detected in the expired gases of mammals. It occurs, however, very abundantly in chemical combination; as with oxygen in the form of water, of which it constitutes one-ninth part by weight, also with carbon in the form of gas—known as marsh gas—that is exhaled from coal-pits; with nitrogen in the form of ammonia; with sulphur as sulphuretted hydrogen; with chlorine as hydrochloric acid, and as a constituent of very many of the substances of which plants and animals are made up.

Characters.—Hydrogen is an elementary substance known in the free state only as a gas which has not as yet been condensed by the greatest cold and pressure combined. It is without colour, taste, or smell; very slightly soluble in water, and burns with a pale bluish flame. Hydrogen is the lightest substance known. Its specific gravity, air being taken as unity, is 0·069. Under normal atmospheric pressure, and at the temperature of 0°, a litre of hydrogen weighs only 0·0896

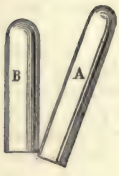


Fig. 4.



Fig. 5.



Fig. 6.

gram. It is therefore possible to decant hydrogen from a cylinder (A) filled with it into another cylinder (B) in the way described by figs. 4 and 5. As soon as the cylinder (A) is placed, with the aperture upwards, vertically under the cylinder (B), all the hydrogen will rise into the upper cylinder, as may be shown by inserting a burning taper into B. The flame of the taper sets fire to the hydrogen at the mouth of the cylinder, where the gas is in contact with the air, but if the taper is raised further up the cylinder, into the pure hydrogen, the flame is at once extinguished. When the extinguished taper is withdrawn, it is again lighted at the mouth of the cylinder by the burning hydrogen gas.

This experiment proves also that hydrogen cannot burn without a supply of oxygen from the air or otherwise, and that the flame of burning bodies is extinguished in pure hydrogen gas.

In setting fire to hydrogen gas, it is necessary to proceed with caution; for if the

gas becomes mixed with atmospheric air, a mixture may, under certain conditions, be produced which, on contact with flame, will explode with great violence, shattering the vessels in which it is contained.

Preparation.—The methods generally employed for obtaining hydrogen depend either upon the decomposition of water by any easily oxidisable metal, or upon the fact that hydrogen is readily displaced from some of its saline compounds. Thus hydrogen can be prepared by passing steam over iron filings heated to redness in an iron tube. The steam is generated in a glass flask with a delivery-tube fitted air-tight into the iron tube. At the other end of the iron tube is fitted another delivery-tube, by which the hydrogen is collected over water or mercury.

The reaction that takes place in this case is easy to understand: iron at a high temperature deprives water of its oxygen, and thus, becoming oxidised itself, the hydrogen is liberated. The first portion of gas evolved contains the air with which the apparatus was originally filled, and therefore this must be allowed to escape, in order to obtain pure hydrogen. If the hydrogen gas be desired free from moisture, it must be passed through tubes filled with pieces of fused calcium chloride, and then collected over mercury. Generally a simpler process is employed in the laboratory. Some granulated zinc is placed in a three-necked bottle (A, fig. 7), of about a litre capacity, nearly half-filled with water. In one tubulus of the flask is fitted with a cork a funnel tube (*b*) reaching to the bottom of the flask; in the other tubulus is fitted one end of a bent delivery-tube (*c*), the other end dipping into a pneumatic trough (E), under the level of the liquid contained in the trough. Above this end of the tube a vessel (D) filled with water is placed in an inverted position on a shelf. The apparatus being thus arranged, concentrated sulphuric acid is poured carefully in small quantities at a time through the tube (*b*), when a brisk evolution of gas commences at once. This evolution of gas may be so violent if too much sulphuric acid be added at once that the liquid in A overflows. By a regular development the hydrogen escapes through the delivery-tube (*c*) and is collected in D. In this case also the first portion of the gas contains the air which originally filled the apparatus, and it must be allowed to escape. Even then the hydrogen obtained by the action of zinc upon sulphuric acid is never quite pure, as shown by the unpleasant smell of the gas, pure hydrogen being absolutely inodorous. This smell is due to admixtures of various kinds, especially hydrocarbons, formed from carbon contained in the zinc; also to the presence of arseniuretted and sulphuretted hydrogen, originating from arsenic and sulphur in the zinc, and from arsenical sulphuric acid.

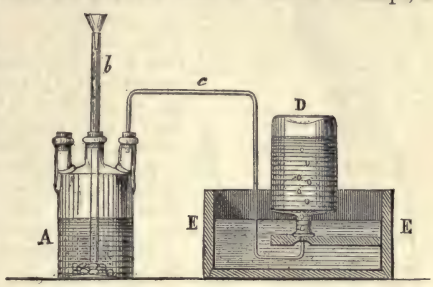


FIG. 7.

Hydrogen can be freed from these impurities by passing it first through a tube filled with pieces of pumice-stone saturated with concentrated solution of caustic potash, then through a tube containing pumice-stone saturated with solution of corrosive sublimate. The impurities are retained by the potash and corrosive sublimate. If the purified hydrogen be required dry, it must then be passed through a tube containing pieces of fused chloride of calcium, or pieces of pumice-stone saturated with concentrated sulphuric acid, before it is collected for use, and in that case the gas must of course be either collected over mercury or at once conducted into the apparatus where it is to be used. The gasholder, described on page 20, is as well suited for hydrogen as for oxygen. From such a gasholder the gas can be transferred to flasks and cylinders at pleasure, or it can be passed in a regular stream into the apparatus where it is to be used.

The process which takes place in this preparation of hydrogen consists in the substitution of zinc for the hydrogen of the sulphuric acid, zinc sulphate being thus formed and hydrogen set free in the state of gas, according to the following equation:

$$\begin{array}{rcrcrcl} H_2SO_4 & + & Zn & = & ZnSO_4 & + & H_2 \\ 98 & + & 65 & = & 161 & + & 2 \\ & & 163 & & 163 & & \end{array}$$

In this equation no account is taken either of the water, which must be added in great excess, in order that the sulphate of zinc formed may be dissolved, or of the excess of sulphuric acid, which is contained in the liquid when it no longer evolves hydrogen by contact with zinc.

Hydrogen can be obtained more readily by means of an apparatus in which the development of gas is regulated by the quantity consumed. An apparatus of the kind is represented by fig. 8. A is a glass vessel furnished with a tubulus (*b*), to which is fitted a cock (B). This vessel (A) is three parts filled with dilute sulphuric acid (1 : 5). Into its neck a large globular glass vessel (C), with a long tube gradually narrowing towards its lower extremity and reaching nearly to the bottom, is fitted air-tight. A thick ring of zinc (*d*) is fastened at the lower end of C, and is held fast by means of a cork placed at the extremity of the tube.

While the zinc is immersed in the acid, hydrogen is developed, and collecting in the upper part of the vessel (A) presses the liquid into the globular vessel (C), from which the air escapes by the neck, as the stopper H is only lightly fitted into it.

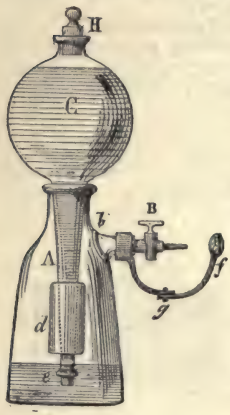


Fig. 8.

In proportion as the liquid is forced up into the globe (C) so its level sinks in the flask (A); and when it has sunk to about *e*, the acid being no longer in contact with the zinc cylinder (*d*) no more hydrogen can be evolved. Then, if the cock (B) be opened, the liquid, which was driven up into C by the pressure of the evolved hydrogen gas, presses out the gas through the cock (B). In proportion as gas escapes from B, the liquid again falls from C into A, until it again comes into contact with the zinc cylinder (*d*), and continues to develop gas so long as the cock is allowed to remain open. But as soon as the cock (B) is closed the hydrogen generated presses the liquid anew into the glass globe (C), until the acid is out of contact with the zinc, and the evolution of gas ceases.

For the preparation of hydrogen on a large scale—as, for instance, in the manufacture of aniline, where large quantities of nascent hydrogen are required, and for like purposes—crude acetic acid and old iron are employed with advantage. The action of iron upon acetic acid is entirely analogous to the action of zinc upon sulphuric acid; the iron displacing the hydrogen of the acetic acid, and forming ferrous acetate. In like manner hydrogen is evolved when zinc or iron is brought into contact with solutions of caustic potash or soda.

Uses.—One of the chief purposes to which hydrogen gas is applied is the production of an extremely high temperature by its combustion with oxygen. The amount of heat generated in the combustion of hydrogen gas, viz. 33,881 heat units for each kilogram of hydrogen burnt (=60,986 British heat units per pound) exceeds that produced in the combustion of any other substance, and when the combustion is supported by oxygen gas the flame has a temperature of more than 6000° C.

Oxyhydrogen Blowpipe.—In consequence of the gaseous condition of hydrogen it can be conveniently burnt so as to produce a small flame of extremely high temperature. Sometimes hydrogen is, for this purpose, mixed with half its volume of oxygen, and compressed in a strong iron vessel furnished with a tap and jet by which the mixed gases can be allowed to escape and burn as required. More frequently, however, a jet of oxygen is mixed with twice its volume of hydrogen immediately before issuing from the jet where the mixed gas is burnt. A piece of lime brought into the oxyhydrogen flame is heated to whiteness and yields a light nearly as bright as the electric light.

This intense light is employed in the illumination of microscopic objects, and is called the Drummond or Oxyhydrogen Lime Light.

Doebereiner's Lamp.—When a jet of hydrogen is made to impinge upon a ball of spongy platinum the combination of the gas with oxygen takes place at the ordinary temperature and the platinum ball is made red hot by the heat thus generated. From an apparatus of similar construction to that shown in fig. 8, it is possible to direct a jet of hydrogen gas, through the cock (B), upon a piece of spongy platinum (*f*), fastened to the holder (*g*) by means of platinum wire. This holder has at *g* a joint by which the spongy platinum may be turned aside when not required to be used. If the spongy platinum be brought exactly opposite to the cock (B), and this is opened, hydrogen escapes, and coming into contact with the spongy platinum, renders it red hot and takes fire.

Autogenous soldering.—The flame of a jet of hydrogen is much used for uniting the edges of the sheets of lead with which vessels are made for the purpose of holding acids. Joints made in this way are more durable than those made with solder.

The soldering apparatus is constructed on the same principle as that represented by

fig. 8, except that it is made of copper-plate lined internally with lead, and fitted with arrangements which admit of the easy renewal of the zinc, the removal of the sulphate of zinc formed, and the replenishing of the apparatus with fresh sulphuric acid. This apparatus gives a very constant flame, which can be used with advantage for soldering lead in the manner practised in constructing sulphuric acid chambers.

It consists essentially of three parts, a gas-generator, a bellows, and a jet. In fig. 9, A, the lower compartment, represents the vessel for generating hydrogen gas. It is made of sheet copper lined with lead. Pieces of zinc are placed upon the perforated bottom (L) through a side door. When the zinc has been thrown in this door is closed hermetically, the stopper (D) taken out, and the copper reservoir filled with sulphuric acid diluted with eight or nine times its volume of water. The union of the flexible tube (*g g*, fig. 11) is then connected with the gas generator at C, fig. 9, and the tube (*g' g'*, fig. 11) with the bellows, fig. 10, at *f*. Both the tubes (*g g* and *g' g'*) are connected together by means of the copper tube (*d' d'*), fitted with another piece of flexible tube (*c c*), terminating in the blow pipe mouth-piece (*b a*) of bronze, or platinum. When this apparatus is required for soldering the cocks (*f*, fig. 9, and *f*, fig. 11) are opened; the air from the interior of the apparatus then escapes through them in proportion as the sulphuric acid entering through G H (fig. 9), rises in the lower division of the gasholder. When the level of the sulphuric acid in this lower vessel has risen higher than the perforated bottom (K L), hydrogen gas is generated and passes through the cock (*f*) and the tube (*b a*), into the small wash vessel B, containing either a small quantity of water or a solution of caustic soda for the retention of any particles of sulphuric acid that may happen to be carried over with the gas. The hydrogen generator having been in operation a short time, a workman sets the bellows in motion with his foot by means of the pedal (*o*). This causes the two ends of the bellows to be pressed together towards their centre, and the air to be forced out through the tube (*g' g'*, fig. 11). The cocks (*f* and *f'*) must be so regulated that the mixture of hydrogen and air gives a finely-pointed flame. So long as the cocks remain open, hydrogen gas continues to be generated. When the soldering operation is finished and the apparatus is no longer required, the cocks

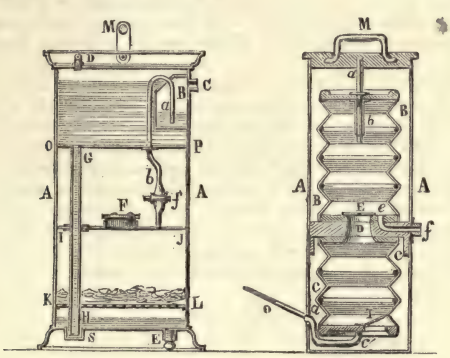


Fig. 9.

Fig. 10.



Fig. 11.

(*f*, fig. 9, and *f*, fig. 11) are closed. The closing of these cocks puts a stop to the further development of gas, since the pressure exerted by gas in the interior of the apparatus causes the sulphuric acid to rise through G H into the uppermost vessel, leaving the zinc out of contact with the acid; the hydrogen gas consequently ceases to be evolved. When the apparatus is again required for use it is only necessary to re-open the cocks and set the bellows in motion as above described.

When the sulphuric acid is nearly saturated with zinc sulphate it is drawn off through the opening at E, and fresh acid poured into the apparatus at D. After each fresh re-charging of the apparatus, whether it be with acid or zinc, air finds its way into the interior of the apparatus and forms with the hydrogen gas an explosive mixture. On this account it is necessary after each re-charging to allow the gas to escape for a few minutes from the mouth-piece of the blowpipe (*c a*, fig. 11), before igniting it, dangerous explosions being apt to occur from a neglect of this precaution.

Air Balloons.—The first air balloons were raised by means of heated air, and had a

very irregular uncertain motion, owing to the unequal heating. It is only since the gases specifically lighter than atmospheric air have been used for filling balloons that it has been possible to secure a more regular motion.

Hydrogen was at one time employed for this purpose, and produced by the action of iron upon a dilute acid. In order to fill a balloon of 500 cubic metres capacity 1,500 kilograms of scrap-iron are required, as free as possible from oxide, 15,000 kilos of water, and 2,500 kilograms of sulphuric acid. As a by-product, a solution is obtained from which, by means of evaporation, crystallising, and drying, about 7,500 kilograms of green vitriol (ferrous sulphate) can be gained.

Assuming that 1 cubic metre of hydrogen weighs 89·6 grams, and 1 cubic metre of atmospheric air weighs 1,293 grams, the rising power which a cubic metre of hydrogen exerts is equal to 1203·4 grams. If the total difference between the weight of the hydrogen and the weight of the same volume of atmospheric air be greater than the weight of the covering and the other solid parts of the balloon, the balloon rises, and rises the quicker the greater this difference is in proportion to the weight of the covering, etc.

More recently, ordinary illuminating gas made from coal has been used for inflating balloons, but since this gas is about six times as dense as hydrogen gas, the balloons filled with it must be much larger. Small balloons consisting either of goldbeaters' skin or very thin caoutchouc, either globular, oval, or in the shape of different animals, etc., can be filled with hydrogen in the same manner. Such small balloons only remain a short time suspended in the air, because diffusion takes place through the membranes or the caoutchouc covering, hydrogen passing out.

Compounds.—Hydrogen forms a number of important compounds with other elementary substances.

There are two compounds of hydrogen and oxygen, the monoxide, or water, which is in many respects one of the most important substances in nature, and the dioxide or peroxide, which contains relatively to hydrogen twice as much oxygen as water.

With nitrogen it forms ammonia NH_3, and with phosphorus, arsenic, and antimony the analogous compound PH_3; AsH_3; SbH_3. With carbon it forms a great number of compounds termed hydrocarbons. Several of the compounds of hydrogen with fluorine, chlorine, bromine, iodine, and sulphur correspond in their chemical relations to the hydrogen salts of acid oxides. On this account they are distinguished, as forming a particular class of acids, by the term hydroacids, and like oxyacids they are largely employed for various purposes. With some of the metals hydrogen forms compounds termed hydrides.

But though hydrogen is a constituent of so many compounds, its chemical activity is but slight under ordinary conditions of temperature, and it combines directly only with chlorine and oxygen. For its combination with oxygen a considerable elevation of temperature is necessary, but when the union of the two gases is once commenced, as in lighting a jet of hydrogen, the heat generated by the combination determines its continuation. Hydrogen combines more readily with chlorine, and when a mixture of these gases is exposed to direct sunlight they combine with explosion. Other compounds of hydrogen with elementary substances are obtained indirectly, and several of them that are of especial value in the arts will be described in the following pages, under the heads of the particular elementary substances they contain.

WATER.

Formula H_2O. Molecular Weight 18.

History.—Thales held water to be the principle, or element, from which all other substances were formed, and still later water was regarded as an elementary substance, constituting one of the four elements of Aristotle: water, fire, air, and earth. The opinion that water could be converted by means of heat into earthy or solid substances was also long prevalent. Cavendish first demonstrated the fact that water consists of hydrogen and oxygen.

Occurrence.—Water occurs naturally in the solid, the liquid, and the gaseous conditions. In the solid condition water is known as ice, snow, or hail; in the liquid condition water occurs as sea, river, spring, mineral, and rain water, etc.; and besides the absolute gaseous condition of water, it occurs in the form of steam, a peculiar intermediate stage between the gaseous and the liquid conditions.

Atmospheric air always contains at the ordinary temperature a considerable quantity of water vapour or gaseous water. The amount varies according to the temperature and the direction of the wind. On the average, it may be assumed that the air

contains 0·8 per cent. by weight of water. This water is a very necessary constituent of the air, for neither animals nor plants are able to live in absolutely dry air. By reduction of the temperature of the atmosphere the water vapour is condensed and receives then the appellations cloud, fog, rain, snow, hail, and frost.

Water also exists in vast quantity, chemically combined in mineral substances, as water of hydration or of crystallisation. It constitutes a large part of the mass of all organic structures. The soft organs of animals contain generally more than three-fourths of their weight of water; the young parts of plants from 80 to 90 per cent.; indeed, there are plants which contain as much as 95 per cent. of water. The thickest trunks of large trees at the time of felling always contain as much as 45 to 55 per cent. of water.

Composition.—Water is a compound of hydrogen with eight times its weight of oxygen, the volume of the oxygen in the free state being half that of the hydrogen. The relation by volume of the constituents of water can easily be proved either by exploding in a suitable vessel a mixture of hydrogen with half its volume of oxygen, whereupon all the gas disappears and water alone is formed, or by decomposing water electrolytically and collecting the gases evolved. In this latter process the volume of the hydrogen evolved is exactly double that of the oxygen.

Characters.—In a chemically pure condition water is colourless; it is only in thick masses that it appears of a faint greenish-blue colour. It is odourless and tasteless; it attains its greatest density at a temperature of + 4° C., and forms in this respect an exception to the general rule that liquids become denser as the temperature is reduced, until they assume the solid state. Cooled to 0° C., water congeals to ice. From the moment when a few crystals of ice are formed, the temperature of the still liquid water does not, in spite of strong refrigeration, sink any further, until the last drop of liquid water is converted into ice. On the other hand, though heat be applied to water in which solid ice is immersed, its temperature does not rise above 0° until the last particle of ice is melted. Under certain conditions it is possible to retain water in the liquid state at a temperature below the freezing point. If kept perfectly at rest, and cooled slowly down to a temperature below 0°, it sometimes remains liquid even at − 12° C. So soon, however, as water thus cooled is set in motion, it congeals suddenly throughout its entire mass to a lump of ice.

The fact above mentioned, that water has its greatest density at + 4° C., and that consequently in becoming ice it again expands, is one of the highest importance as regards the upper stratum of the earth's crust. The disintegration of rocks is due in part to this property of water, for since water penetrates into their pores and crevices as into a sponge, its expansion upon becoming ice is sufficient to disintegrate the most compact rocks. So long as the ice thus formed continues to serve as a connecting material, these fragments are held together by it, but upon the setting in of a thaw, the ice melts and the rocks fall to pieces.

On account of the great force with which water expands in its transition to ice, vessels, made of a brittle material, when left in the cold filled with water, are liable to be burst by the formation of ice within them.

As ice occupies a greater space than an equal weight of water at 0°, it follows that ice is specifically lighter than water. The fact that ice floats upon water is certainly one of great importance. If ice were heavier than water, it would sink to the bottom from the surface of brooks, rivers, seas, etc., upon which it was formed by the cold of winter, a new ice crust would be formed, which would also sink to the bottom, and so on, in consequence of which the brooks, rivers, seas, etc., would very rapidly freeze up. But since ice is lighter than water, it forms a sheltering cover for the water underneath it.

The form of ice crystals is difficult to ascertain, as such crystals are generally imperfectly formed. The best way of observing that ice crystals are six-sided prisms is the examination of the arborescence which forms on window-panes in winter.

Water boils at a temperature of 100° C. under the normal atmospheric pressure, equal to a column of mercury 760 mm. in height, and, with the phenomenon of bubbling, it is converted into the gaseous condition. The temperature at which water boils is lower in proportion as the pressure exerted upon its surface is reduced. Therefore, since the pressure of the atmosphere is less upon the top of high mountains than in valleys or at low levels, water boils at a much lower temperature at considerable elevations. Upon the top of Mont Blanc, for instance, where the atmospheric pressure is only equal to a column of mercury 423·7 mm. high, water boils at a temperature of 84·4° C. In a vacuum it boils at 0°. Owing to the tension of water vapour, water assumes the gaseous state at a temperature below its boiling point, and the vapour diffuses into spaces filled with other gases that are indifferent to it. This tension is the cause of water being always present in the atmosphere in the form of gas or vapour. The

evaporation of water is more considerable the greater the surface exposed, and the higher the temperature of the water and of the surrounding air. Thus cold air saturated with water vapour is capable of absorbing a fresh quantity when warmed, and on the other hand warm air saturated with water deposits the water in the liquid state when cooled. Hence it is that cold objects become covered with moisture when brought into contact with warm air—as, for instance, the glasses of spectacles when a person enters a warm room, or the window-panes of heated rooms.

Certain solid and liquid substances, such as calcium chloride or magnesium chloride, dry potassium carbonate, concentrated sulphuric acid, etc., possess the property of withdrawing water from moist air, while at the same time they dissolve in the water thus attracted. These substances are, therefore, termed deliquescent. Other substances, on the contrary, which upon crystallising have taken up much water—*e.g.* sodium sulphate, carbonate or phosphate—give up a portion of their water when exposed to the air, losing their crystalline form and falling to powder. These are called efflorescent substances. Many solid substances also attract moisture from the air without dissolving and are for this reason termed hygroscopic. Organised substances, such as wool, hair, etc., and many pulverulent substances, present this character in a marked degree.

Water is a general solvent. As a rule, it dissolves a given substance in greater proportion the higher its temperature is. Still there are exceptions to this rule—as, for instance, Glauber's salt, the solubility of which in water increases only to a definite degree of temperature, and upon further elevation of the temperature decreases. In consequence of the solubility of most substances in water being greater the higher the temperature is, hot saturated solutions deposit upon cooling a portion of the substances dissolved, for water at a low temperature is not capable of dissolving the same quantity of a salt as water of a higher temperature, and, as a rule, the substances deposited in this way assume the crystalline form.

Water dissolves, or, as it is generally expressed, absorbs, less of a particular gaseous substance the higher its temperature is. In like manner, water absorbs less of a gas the smaller the pressure is with which the gas presses upon the surface of the water.

Natural Water.—Water, as it occurs naturally, is never chemically pure, on account of its great solvent power; and since it is always in contact with other substances, which it dissolves; even the potable water of springs, wells, reservoirs, or brooks, always contains in solution varying amounts of foreign substances. These consist of oxygen, nitrogen, and carbonic acid gases; alkaline and earthy salts, chiefly carbonates and sulphates, and chlorides of potassium, sodium, and magnesium, together with traces of organic substances and silicic acid.

Rain or snow water, as it falls, is generally contaminated only with the gases contained in the atmosphere. Only that water which falls when it first begins to rain contains the dust always to be found in the air that is in motion.

This rain or snow water is in part retained in the earth by its porosity, conveying to the roots of plants the constituents of the soil necessary for their nourishment; another part penetrates deeper into the earth, saturating itself with the soluble constituents of the earth's crust through which it passes, and then collects again in the form of streams and rivers, along the course of which it flows into the sea. Here, and partly also from the moist surface of the land, it is evaporated by means of the heat of the earth and the sun, and the evaporated water, on reaching high cold regions of the atmosphere, is again condensed, and falls once more in the form of rain, etc., upon the earth.

Well water is water which accumulates above an impermeable stratum, generally of clay at little depth below the surface. Such water is termed hard when it contains in solution large amounts of calcium carbonate or sulphate. Calcium carbonate is retained in solution by means of carbonic acid, for it is dissolved in far larger proportion by water containing free carbonic acid than by water free from that substance. If, however, water of this kind be boiled, the solvent agent, the carbonic acid, is expelled in the form of gas, and carbonate of lime is then precipitated in the solid state, the water becoming turbid. In like manner, on evaporating water, all other salts dissolved in it are deposited, and the more readily the less soluble they are, forming the scale of boilers.

Spring water is essentially the same as well water, only that, by flowing along steep impermeable mountain strata, it finds an outlet for itself where these strata crop out at lower points of the earth's surface, and thus appears in the form of springs.

The various kinds of mineral water are spring water, holding in solution substances to which their especial medicinal properties are due. Thus, sulphuretted water contains sulphuretted hydrogen; acidulous water contains much carbonic acid; and bitter water contains magnesium sulphate, sodium sulphate, etc.

There are besides these some kinds of mineral water the action of which is due to the temperature at which they issue from the earth. The water of the hot springs at Carlsbad has a temperature of 74°, that of the springs of Baden-Baden 71½°, those of Wiesbaden of 70°, those of Teplitz 49½°, and those of Vichy of 45½°.

River water is generally soft, though originating from spring water—*i.e.* it does not contain in solution any large amount of calcareous salts. This is owing to the fact that spring water, by long contact with the atmosphere, loses the greater portion of its carbonic acid, and consequently deposits its calcium carbonate together with traces of calcium sulphate. For the same reason river water tastes insipid as compared with the fresh-tasting well or spring water, which still contains carbonic acid.

Sea water differs from ordinary potable water in the large proportion of saline substances contained in it. It contains over 3½ per cent. of salts in solution, amongst which common salt preponderates.

The average composition of sea water is as follows:

Water		96·470
Sodium chloride (common salt)	2·700	
Potassium chloride	0·020	
Magnesium chloride	0·360	
Calcium sulphate (gypsum)	0·140	
Magnesium sulphate	0·240	3·530
Potassium sulphate	0·005	
Calcium and magnesium carbonates	0·004	
Bromine and iodine compounds, together with organic substances	0·011	
Carbonic acid and volatilisable organic substances	0·050	
		100

The composition of sea water is not everywhere the same. The water of the Mediterranean Sea, for instance, contains less magnesian salts than the water of the ocean, and at great depths sea water is salter than near the surface.

In the Dead Sea, the amount of salt varies considerably according to the depth. In the following table are given the results of analyses by Terreil. In the first column the constituents of the water at the surface of the Dead Sea are given, in the second the constituents of the same water at a depth of 1,000 feet.

1,000 parts of water contain	Minimum at the surface	Maximum at the depth of 1,000 feet
Chlorine	17·628	174·985
Bromine	0·167	7·093
Sulphuric acid	0·202	0·523
Carbonic acid	traces	traces
Sulphuretted hydrogen	traces	traces
Magnesium	4·197	41·428
Calcium	2·150	17·269
Sodium	0·885	14·300
Potassium	0·474	4·386
Ammonia, alumina, oxide of iron, organic substances	traces	traces
Silicon	0·006	traces
	25·709	259·984
Residue directly determined	27·078	278·135
Water	972·922	721·865

It is evident from this that at a depth of 1,000 feet most salts in the water of the Dead Sea are contained in solution in a ten times greater amount than at the surface.

The large quantities of bromine and of potassium salts contained in the water of the Dead Sea admit of the probability of the Dead Sea being worked at some future period for those substances.

Salts of calcium and magnesium in water communicate to it the power of forming an insoluble curd with soap, and render the water hard; the greater the amount of these substances, the harder is the water.

When the saline substances are present only in moderate proportion, as in river water, their presence is not objectionable for most of the purposes to which water is applied; indeed these substances render water more pleasant to drink, and perhaps they may in some degree contribute to nutrition.

In household economy and for manufacturing purposes the water most often used is spring, well, or river water; in dry countries, rain water is collected in tanks.

An idea of the characters of natural water in this respect is given by the accompanying table of analyses.

In judging of the quality of water, account is to be taken of its hardness, its temperature, and its purity. It is also of importance to determine whether the hardness is due to earthy carbonates or to the corresponding sulphates and chlorides. In the former case, if the water be allowed to remain for a short time with a considerable surface exposed to the air, the greater part of the calcium and magnesium carbonates are gradually deposited, owing to the escape of the carbonic acid which determined their solution by the water, and thus the water becomes softer. Such water is also rendered soft by boiling. On the contrary, if calcium and magnesium are present in the state of sulphates or chlorides, the water remains hard after exposure to the air, as well as after boiling. Hence it is easy to understand the reason why many kinds of spring water which are very hard when first escaping from the earth, afterwards become soft when they have flowed for a certain distance down a brook or river. In such cases the carbonic acid escapes, and consequently the carbonates which caused the hardness of the water are deposited in the form of mud.

Good potable water should be clear, colourless, cool, and clean—*i.e.* it should be free from mechanically suspended impurities, such as clay, organic substances, etc.; it should contain in solution small amounts of the acid calcium carbonate, common salt, with nitrogen and oxygen gases, and especially carbonic acid. The presence of other compounds of calcium and magnesium than the carbonates is detrimental in proportion to the amount of those substances.

Good potable water may contain in 100,000 parts from 10 to 30 parts of solid contents that remain behind when the water is evaporated, and one half of the solid contents may consist of calcium carbonate. If water contains less than 10 parts of solid contents per 100,000, it is too soft, and is less suitable as potable water than water that is richer in salts. For this reason, rain water is not good for drinking. As regards the aëration of potable water, it ought to contain by measure about 0·8 per cent. of oxygen, 1·7 per cent. of nitrogen, and besides these gases a considerable quantity of carbonic acid.

For industrial purposes soft water is generally preferable. For certain purposes, however, such as the dyeing of some colours, hard water is more suitable. For other purposes, it is a matter of indifference whether water be hard or soft. For cooling purposes, that water would be chosen which indicated the lowest temperature. Hard water is not at all suitable for steam boilers, on account of the formation of scale by the deposition of its solid contents in the boiler. In this respect also, the state of combination in which the calcium exists is a matter of great moment: calcium carbonate and calcium chloride are comparatively harmless, the latter being very soluble, and the former producing a scale of a loose nature which is easily removed, while calcium sulphate (gypsum) gives rise to a very hard and adhesive scale, and when present in any considerable quantity in water renders it utterly useless for steam boilers unless it is submitted to a process of purification beforehand.

Purification.—In many cases it is necessary to adopt some means of separating impurities from natural water, to render it suitable for use.

A very efficient method of preventing this objectionable action of gypsum consists in the addition of sodium carbonate (common soda), which converts the gypsum into calcium carbonate, that is deposited in the state of mud and not as a hard scale; for every degree of hardness of water rich in gypsum, about 5 parts of soda crystals, or 2 parts of calcined soda, are added to each 100,000 parts of water. Barium chloride has also been proposed for the decomposition of gypsum, and by its use water very suitable for steam boilers can be obtained. But at present this salt is too dear for the purpose. Sal-ammoniac would be applicable for preventing the formation of scale by water containing gypsum, were it not that the steam might become ammoniacal, and then act injuriously upon the working parts of the steam engine. Substances containing tannin have been found very serviceable for this purpose, and have lately been much used. Decoction of oak bark has been used, and more recently catechu.

If it be desired to get rid of the hardness of water for washing, all the calcium salts held in solution must be precipitated. This is most easily effected by the use of common soda, whereby all the calcium is precipitated as carbonate.

Filtration.—Muddy water can be easily rendered clear by filtration. In places

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	KCl	Nitrates $Ca2NO^3$	$Mg2NO^3$	$NaNO^3$	KNO^3	SiO^2	Al^2O^3	Fe^2O^3	Organic substance
Thames	·96	·38	—	—	—	·88	·14		3·27
„	—	—	—	—	—	·39	—	—	4·97
„	—	—	·50		—	1·09	—	·49	2·20
„	·33	—	—		—	·18	trace	trace	10·00
„	—	—	—		—	1·13	—	„	5·82
Rhine at	—	—	—	—	—	·19	·14		—
„ at	—	—	—	—	·38	4·88	·25	·58	—
„ at	·45	—	—	—	—	·89	—	·28	—
Seine ab	—	—	—	trace	—		·80		trace
„ be	—	—	—	„	—		2·40		„
Rhône a	—	—	—	·85	—	2·38	·39		—
„ a$_s$	—	—	—	—	—	trace	—		trace
Spree at	—	—	—	·30	—	—	1·3		—
Maes at	—	—	—	—	—	·28	·23		—
„ at	—	—	—	—	—	2·00	·50		trace
Elbe nea		—	—	—	—	·54	·12		—
Exe nea	trace	—	—	·23	—	trace	—	—	2·30
Dee near	·96	—	—	—	—	·20	—	—	2·60
Aar nea	—	—	—	—	—	·27	—	trace	trace
Arve (F	—	—	—	—	—	·20	—	—	·40
„ (A	—	—	—	—	—	·10	—	—	·20
Doubs .	—	—	—	·80	—	1·59	—	trace	—
Marne .	—	—	—	—	—	·60	—	—	trace
Bièvre n	—	—	—	—	—	—	—	—	—
Ouroy n	—	—	—	traces	—	2·00	—	—	trace
Yonne n	—	—	—	—	—	1·90	—	—	„
Beuvron	—	—	—	—	—	—	—	—	—
Théroue	—	—	—	—	—	—	—	—	—
Gergogn	—	—	—	—	—	—	—	—	—
Vesle ne	·22	—	—	—	—	·18	·11	·36	·79
Lütschin	—	—	—	—	—	·35	·10	—	—
Möll, nea	·09	—	—	—	—	·72	trace	·10	—
Oetz nea	—	—	—	—	—	·86	„	—	—

where the only available water is muddy, it is purified in filtering tanks. These consist of large water-tight basins at the bottom of which is placed a layer of coarse stones, over this a layer of coarse sand or gravel, then a layer of fine sand, and on the top a layer of river sand. The water is led in above, and filters through the several layers, collecting in the lowest one. From thence it passes into reservoirs or shafts built vertically in the basin, and having their walls so perforated at the lower part, where they are in contact with the coarse stones, that only filtered water can enter them. The filtered water is pumped out from these reservoirs, and conducted to its destination. Iron tubes perforated below are often used instead of brickwork reservoirs. The greater portion of the suspended impurities contained in the water is retained in the uppermost layer of sand, and consequently this has to be renewed from time to time.

By filtering water through powdered charcoal, not only are mechanically suspended substances got rid of, but substances that are present in solution are also removed to some extent—for instance, foul gases, and decaying organic substances—and in this way water coloured by such substances may often be rendered colourless. However, the charcoal soon becomes saturated with the absorbed substances, and rendered useless, so that filtration through charcoal cannot be conducted advantageously on a large scale. It may even happen that charcoal which has become thus saturated at a low temperature will give up a portion of the absorbed substance when the water to be filtered has a higher temperature. On a small scale, however, carbon filters in various forms are frequently used for purifying water.

At present no means are known of rendering sea water potable by simple filtration. Many experiments have been made in this direction, but no cheap material has been found capable of retaining the salt.

Distillation.—Water that is to be used for analysis and other chemical purposes must be purified by distillation, for all kinds of natural water are too impure for such purposes; even rain water contains impurities originating from the atmosphere, such for instance as dust, salts of ammonia, etc., which render it unfit for many purposes.

The purification of water by distillation is very simple. For this purpose, the purest natural water obtainable should be selected, and especially that most free from smell. The apparatus in which the distillation is carried out varies in shape and arrangement. Generally it consists of a copper still, heated from beneath so as to boil the water in the still. The steam is conducted, by means of a head, fastened air-tight to the still, into a cooling apparatus, where it is condensed and flows out below. The condenser generally consists of a serpentine tube, fitted into a tub filled with cold water in such a way that the interior of the tube cannot communicate with the cold water surrounding it. The first portion of water which distils over is thrown away, since it contains all the gaseous products which were dissolved in the water. The collection of the distillate is not begun until one-fourth of the water has distilled over, and then, provided the operation has been properly conducted, the distilled water is chemically pure. In purifying water by this method, care must be taken to avoid too violent boiling, by which some of the water from the still might be spirted into the condensing apparatus, and also to prevent the water in the still from being evaporated to dryness, in which case the solid contents, reduced to a dry state, might be decomposed, yielding gaseous products, which would pass into the distillate. In either case the distilled water would be rendered impure.

Distillation of sea water.—In order to obtain pure water from sea water, a plan is adopted similar to that just described, only that in this case greater precaution is necessary. Sea water contains in solution a much greater amount of salts than ordinary well or river water, and upon evaporation these salts form a thick crust in the still, which adheres firmly to the bottom. Consequently, overheating of the bottom of the still easily occurs, whereby on the one hand salts are decomposed, and on the other hand the still itself suffers. This difficulty has to a great extent been overcome by the use of an apparatus, constructed by Dr. Normandy, which is extensively used in ships making long voyages.

The distillation of sea water for the purpose of rendering it potable has attracted the attention of many. The first to occupy himself with the matter was an Englishman of the name of Hanton, and later on, in 1714, a Frenchman named Gautier. Their apparatus, however, was very imperfect, and found on this account no general employment. Peyre and Rochère have recently constructed an apparatus of the kind in which the heat of combustion is not only used for the distillation of water, but at the same time, by means of a suitable condenser, for culinary purposes.

The first and last portions of the distillation are collected separately, and serve for washing purposes. The intermediate portion is used for drinking. This water is

rendered more potable by heating it in a kind of drum in which the air is constantly renewed. By this means the water absorbs oxygen and carbonic acid in the proportion in which these gases are contained in river water. This water would be rendered better and more palatable by adding to it one tenth per cent. of water saturated with calcium carbonate and free carbonic acid.

Uses.—There is no substance that is made use of on so large a scale as water, both in manufactures and in household economy. It is employed for the purpose of transferring heat to other substances which cannot with advantage be submitted to the direct action of fire, either by means of bringing them in contact with hot water, or by the application of steam. Water is used for purposes of purification, for dissolving or crystallising a number of substances, for producing and promoting numerous chemical and physiological changes which set in activity the industrial energy of mankind in manufactories, in agriculture, horticulture, etc. Lastly, water is the substance by means of which heat is converted in steam engines into force.

If all the uses thus cursorily alluded to be considered, it will be evident that there is no substance of more general and higher importance than water.

Compounds.—Water combines with a number of substances in a variety of ways, forming compounds which are generally termed hydrates, though in many instances they probably do not actually contain water, but are to be regarded rather as derivatives of water, by the substitution of elementary or compound substances for a portion of its hydrogen. Thus, for instance, nitric hydrate, or ordinary nitric acid, and sodium hydrate should be represented by the formulæ $\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$ and $\left.\begin{matrix}Na\\H\end{matrix}\right\}O$, as derivatives of water, half of the hydrogen being replaced by the monovalent radicle NO_2, and by the monovalent element Na respectively.

Sulphuric hydrate, or ordinary sulphuric acid, corresponds in like manner to a double molecule of water, and may be represented by the formula $\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$, half the hydrogen being replaced by the bivalent radicle SO_2.

The composition of ethyl hydrate, or ordinary alcohol, and of its analogues, may also be represented as bearing the same relation to water $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$, half of the hydrogen being replaced by the monovalent radicle, or pseudo-metal, ethyl C_2H_5.

A number of carbonaceous substances, such as starch, sugar, etc., containing, besides carbon, hydrogen and oxygen in the same proportions as water, may on that account be regarded as compounds of carbon with water, or hydrates of carbon, and they are often termed carbohydrates; but other considerations give greater probability to the opinion that the constitution of these substances, or the mode in which their elementary constituents are arranged, is very much more complex.

In many compounds, however, some part of the hydrogen and oxygen they contain actually exists as water. This is especially the case with many crystalline salts; for instance, potassic aluminum sulphate $\left.\begin{matrix}2SO_2\\Al_2\\K\end{matrix}\right\}O_4$ is capable of combining with twelve molecules of water, forming the crystalline salt called alum, $KAl_2\,2SO_4\,12H_2O$, containing nearly half its weight of water, which can be separated by heating the salt to redness. Water in this state of combination is termed water of crystallisation.

HYDROGEN PEROXIDE.

Formula H_2O_2. Molecular Weight 34.

Composition.—This compound of hydrogen and oxygen contains relatively to hydrogen twice as much oxygen as water does, and its composition is represented by the formula H_2O_2.

Characters.—Hydrogen peroxide is a colourless liquid, in its outward appearance not distinguishable from water, but very different from that substance in its chemical and physical properties. Its density is almost one-and-a-half times that of water, the specific gravity being 1·45. It does not become solid at −30° C. At a temperature of from 15° to 20° it decomposes, yielding water and oxygen; it cannot, therefore, be converted by means of heat into the gaseous condition, but it can easily be evaporated in a vacuum. Hydrogen peroxide bleaches vegetable colours; and causes violent irritation of the skin; its taste is acrid and bitter. It is soluble in all proportions in water; and is soluble in ether in considerable amount. The ethereal

solution is very stable, indeed hydrogen peroxide will partly distil over with the ether vapour.

Hydrogen peroxide yields its oxygen with readiness to oxidisable substances, and is therefore a powerful oxidising agent. It oxidises arsenic to arsenic acid, phosphorous acid to phosphoric acid, protoxide of iron to peroxide of iron, etc.

Hydrogen peroxide also acts as a reducing agent. If it be brought, for instance, into contact with easily reducible oxides, such as oxide of gold, oxide of silver, or oxide of platinum, evolution of gas takes place, the oxygen of the metallic oxides escaping, together with the half of the oxygen of the hydrogen peroxide, water and metal remaining behind. In the same way, it reduces manganic acid, chromic acid, peroxide of lead, etc., to lower oxides.

Hydrogen peroxide manifests a still more remarkable behaviour with certain other substances. In contact with finely divided platinum, gold, silver, peroxide of manganese, and other finely divided substances, the half of its oxygen escapes, accompanied by a rise of temperature of the whole mass; water remains behind; but the substances which cause this decomposition do not undergo any alteration whatever. Berzelius termed this phenomenon **contact action**.

Some of the reactions of hydrogen peroxide are very marked and admit of its presence being readily detected. Thus, if a few drops of a dilute solution of potassium chromate, with a few drops of dilute sulphuric acid, are added to a liquid containing only minute quantities of hydrogen peroxide, and the whole is shaken with a little ether, perchromic acid is formed, which colours the ether intensely blue. Mere traces of hydrogen peroxide can be detected by adding a small quantity of starch paste containing potassium iodide to the liquid to be tested, together with from two to three drops of an extremely dilute solution of sulphate of iron. The smallest quantity of hydrogen peroxide causes the formation of blue iodide of starch. Of course the liquid to be tested must not contain any substance that likewise produces a blue coloration of starch paste containing potassium iodide.

Preparation.—The preparation of hydrogen peroxide is based upon the fact that certain metallic peroxides—as, for instance, potassium peroxide, or barium peroxide, upon treatment with dilute acids—yield oxygen which is not separated in the free state, but combines with the water present, forming hydrogen peroxide. It is best to use barium peroxide for this purpose. This decomposes with dilute sulphuric acid according to the following equation:

$$BaO_2 + \left.\begin{matrix} SO_2 \\ H_2 \end{matrix}\right\} O_2 = \left.\begin{matrix} SO_2 \\ Ba \end{matrix}\right\} O_2 + H_2O_2.$$

Hydrochloric acid is better suited for this purpose than sulphuric acid, because it forms a soluble salt of barium, which does not hinder the further action of the acid upon the peroxide, as the barium sulphate does. But carbonic acid is the most suitable for the preparation of pure hydrogen peroxide. In order to prepare it by the action of carbonic acid, an abundant stream of the washed gas is passed through distilled water in a beaker. To this water finely-powdered barium peroxide is added from time to time in very small quantities, so that there is never any great excess of barium peroxide present in the liquid containing hydrogen peroxide, which in such case would be decomposed into water, with the evolution of oxygen. After this operation has been carried on for some time the barium carbonate is filtered off, and the solution evaporated in vacuo over sulphuric acid until the liquid assumes a syrupy consistence.

Hydrogen peroxide cannot be preserved long in this condition. In order to preserve it, it must be diluted with water, and made slightly acid with hydrochloric acid. Even in this state, it gradually decomposes, especially when exposed to light.

Uses.—Hydrogen peroxide has been used, according to the recommendation of its discoverer Thénard, for restoring the white colours in pictures that had turned grey or black. It acts in this case by giving off its oxygen, which oxidises the black sulphide of lead and converts it into white sulphate of that metal. In this way the blackened colours of oil-paintings have been restored by making use of water containing only 2 per cent. by measure of hydrogen peroxide. If hydrogen peroxide were cheaper, it might be used with advantage for cloth-bleaching.

Hydrogen peroxide has been used in medicine, but at present only externally.

NITROGEN.

Symbol N. Atomic Weight 14.

History.—Rutherford discovered in 1772 that atmospheric air contains a peculiar gas, which remains when an animal respires in a closed space, and is not capable of supporting either respiration or combustion. Not long afterwards Scheele and Lavoisier ascertained that atmospheric air consists chiefly of this gas, together with oxygen. Lavoisier gave it the name of Azote, and Chaptal called it Nitrogène, because the same gas occurs in nitric acid; hence its designation with the letter or symbol N.

Occurrence.—Nitrogen occurs abundantly in the free state, constituting about four-fifths of the volume of atmospheric air, or rather more than three-fourths of its weight.

It also occurs largely in a state of combination with oxygen and potassium, sodium, or calcium, as a constituent of the corresponding nitrates, saltpetre, cubic nitre, and nitrocalcite. Oxides of nitrogen also exist in small proportion in the atmosphere. Nitrogen in combination with hydrogen occurs as ammonia in the atmosphere, in some kinds of natural water, and in volcanic exhalations. Many substances, such as albumin, casein, etc., that are of great importance in connection with the vital phenomena of plants and animals, contain nitrogen as an essential constituent, and other nitrogenous substances of like origin are remarkable either for their powerful medicinal properties or for their applicability as dyes, etc.

Characters.—Nitrogen gas is characterised by its chemical indifference towards other substances, and it is on this account impossible to separate it from the air by means of another substance. It is colourless, tasteless, and odourless; as compared with hydrogen its density is 14, and relatively to atmospheric air its specific gravity is 0·9713. It has not been possible as yet, by the agency of the most powerful pressure, combined with the most intense cold, to condense nitrogen gas to a liquid condition. Nitrogen gas is slightly soluble in water; at 0°C. the amount dissolved is only a little above 2 per cent. by measure. It is not inflammable; on the contrary, burning substances are immediately extinguished when brought into an atmosphere of nitrogen gas; it is equally irrespirable, for if it does not act as a positive poison upon the animal organism, still animals are suffocated in an atmosphere of the pure gas.

Preparation.—Nitrogen is generally prepared from atmospheric air, of which it constitutes nearly three-fourths by weight. All inflammable substances burn in the air at the expense of the oxygen; therefore if combustion is carried on in a closed space, it continues only so long as oxygen is present. Combustion ceases as soon as all the oxygen is used up, nitrogen and the products of combustion remaining behind. If, for instance, a glass bell jar be placed over a small dish containing a piece of phosphorus, floating upon water contained in a trough, and thus allowed to remain for twenty-four hours, slow combustion of the phosphorus takes place, the products of combustion, phosphorous and phosphoric acids dissolve in the water, and nitrogen alone remains in the bell jar.

In order to obtain nitrogen from the air more speedily, it is convenient to proceed in the following manner: A large flat cork, somewhat hollowed out in the middle, is allowed to float upon the surface of water contained in a pneumatic trough, and upon it is placed a small porcelain dish containing a piece of dry phosphorus. The phosphorus is ignited, and over the whole is inverted a large glass bell jar, in such a manner that the rim at the bottom dips at least an inch deep into the water. The burning phosphorus rapidly withdraws all the oxygen from the air contained in the bell jar, forming phosphoric acid, which fills the jar with white clouds, and gradually dissolves in the water. As the volume of air in the bell jar is diminished, in consequence of the withdrawal of oxygen, the water rises in the jar and occupies eventually the space that the oxygen had previously occupied. Nitrogen obtained in this manner is never absolutely pure, for it contains still the carbonic acid which was contained in the air, as well as a small quantity of oxygen, since the phosphorus ceases to burn before all the oxygen has disappeared.

Pure nitrogen can be obtained by freeing atmospheric air from water-vapour and carbonic acid, and conducting such purified air over ignited metallic copper. For this purpose, a gas-holder, such as that described on p. 20 (fig. 3), is filled with air, which is conducted first of all through a glass U-tube filled with pieces of fused calcium chloride, then through a similar tube filled with pieces of fused potassium hydrate. After the air has by this means been freed from water and carbonic acid, it is passed through a horizontal tube of difficultly fusible glass, filled with copper turnings and heated to redness. In this tube oxygen is absorbed by combining with the red-hot copper, forming oxide of copper, and it is only necessary to collect the escaping gas over water in a suitable vessel in order to obtain pure nitrogen gas.

Nitrogen gas in the pure state can also be obtained by conducting chlorine gas through a solution of ammonia in water. Chlorine deprives part of the ammonia of its hydrogen, forming first of all hydrochloric acid, and this combining with another portion of ammonia, forms sal-ammoniac (ammonium chloride), according to the equation; this method of preparation is attended with some danger in consequence of the possible formation of explosive nitrogen chloride:

$$4NH_3 + 3Cl = 3NH_4Cl + N.$$

Lastly, pure nitrogen gas can be obtained by heating ammonium nitrite in a retort, the delivery tube of which opens under a glass bell jar over water contained in a pneumatic trough. Upon the application of heat to the nitrite, its hydrogen combines with the oxygen of the nitrous acid, forming water, which condenses, and nitrogen is liberated, according to the equation:

$$\left.\begin{matrix}NO\\NH_4\end{matrix}\right\}O = 2\left\{\begin{matrix}H\\H\end{matrix}\right\}O + 2N.$$

Nitrogen is often set free as a by-product upon heating nitrogenous organic substances for various purposes.

Uses.—Nitrogen gas has been employed with advantage for replacing atmospheric air in vessels in which easily decomposible organic substances are preserved. There are a number of substances, especially organic substances, which decompose upon long contact with the air. In order to prevent this, the vessels in which such substances are to be preserved are filled with nitrogen gas. Instead of filling the vessel with nitrogen, the substance to be preserved may be mixed with a substance which on the one hand deprives air of its oxygen, and on the other hand prevents fermentation and decay. Such substances are the sulphides of the alkali metals, sulphurous acid, the proto-salts of iron, certain ethereal oils, etc. In chemical laboratories also, advantage is taken of the chemical indifference of nitrogen, by filling with the gas apparatus which contain easily oxidisable substances.

Compounds of Nitrogen.—Notwithstanding the marked chemical indifference of nitrogen in the free state, many of its compounds are remarkable for their chemical energy.

There are five oxides of nitrogen, three of which form with water or metallic oxides salts, which are respectively termed hyponitrites, nitrites, and nitrates, the several hydrogen salts being commonly called acids. The composition of these oxides and of the corresponding hydrogen and potassium salts is shown in the following table:

Monoxide or nitrous oxide . .	N_2O	Hyponitrous acid .	H_2ON_2O or HNO
		Potassium hyponitrite	K_2ON_2O KNO
Dioxide or nitric oxide . . .	N_2O_2		
Trioxide or nitrous anhydride .	N_2O_3	Nitrous acid . . .	$H_2ON_2O_3$ or HNO_2
		Potassium nitrite .	$K_2ON_2O_3$ KNO_2
Tetroxide or peroxide . . .	N_2O_4		
Pentoxide or nitrihydride . .	N_2O_5	Nitric acid . . .	$H_2ON_2O_5$ or HNO_3
		Potassium nitrate .	$K_2ON_2O_5$ KNO_3

The compound of nitrogen with hydrogen, called ammonia, has a composition represented by the formula NH_3. This substance is the type of a number of substances termed compound ammonias or amines, in the composition of which the place of one or more of the hydrogen atoms in ammonia is occupied by an alcohol radical; one of the most important of these substances, in a technical point of view, is aniline, C_6H_7N, the source from which a great number of dyes are now prepared. It contains, in the place of one of the hydrogen atoms of ammonia, the compound radical phenyl, C_6H_5, its composition being represented by the formula $N\left\{\begin{matrix}H_2\\C_6H_5\end{matrix}\right.$

With carbon, nitrogen forms cyanogen, CN, a substance that is remarkable for its analogy to chlorine, and its pseudo-elementary characters.

The compounds of nitrogen with chlorine, bromine, and iodine, though interesting, are not of technical importance.

Nitrogen appears to form definite compounds with iron, copper, and other metals.

NITROUS OXIDE.

Formula N_2O. Molecular Weight 44.

Composition.—This substance contains rather more than one-third its weight of oxygen. The normal volume of nitrogen is double that of the oxygen, and the joint volume of the gases is condensed one-third in combination.

Characters.—Nitrous oxide is, at ordinary temperatures, a colourless gas, having a faint odour and sweet taste. Its density is 22 as compared with hydrogen, and relatively to air its specific gravity is 1·525. At 15° it dissolves in rather more than its own volume of water, and at 0° in less than its volume. It condenses to a liquid under a pressure of about 50 atmospheres, and more readily when cooled to 0°. In the liquid state nitrous oxide has a specific gravity of 0·9 and by cooling to −99° it solidifies.

Nitrous oxide gas supports combustion; but less actively than oxygen, and it can be readily distinguished from oxygen by its greater solubility in water.

Preparation.—Nitrous oxide is formed by the action of zinc upon a mixture of equal parts of nitric acid and sulphuric acid; but the best method of preparing the gas is to heat ammonium nitrate NH_4NO_3 in a glass flask to a temperature not exceeding 250°, when the salt melts and is decomposed according to the following equation, giving off the gas with the appearance of ebullition.

$$NH_4NO_3 = 2H_2O + N_2O.$$

On account of the solubility of the gas in cold water, it must be collected over mercury or warm water or a solution of salt.

Uses.—Nitrous oxide, when inhaled, produces temporary insensibility, and on this account it is used as an anæsthetic in surgical operations.

Compounds.—Nitrous oxide forms a series of saline compounds called hyponitrites, which are very instable and can be obtained only indirectly by the reduction of nitrates.

NITRIC OXIDE.

Formula NO or N_2O_2. Molecular Weight 30 or 60.

Composition.—This substance contains nearly half its weight of oxygen, and is a compound of nitrogen and oxygen in equal atomic proportions. The normal volumes of the constituent gases are equal, and they are combined without condensation.

Characters.—Nitric oxide is a colourless gas, that has not been liquefied by cold or pressure. Its density is 15 as compared with hydrogen, and relatively to air the specific gravity is 1·039. Nitric oxide is very sparingly soluble in water, which takes up only about one-twentieth of its volume of the gas; but it is copiously dissolved by solutions of ferrous salts, forming a brown liquid which absorbs oxygen from the air. Nitric acid also dissolves the gas, forming a blue, green, or brown liquid, according to the concentration of the acid.

Nitric oxide is a very stable compound, and when dry it is not decomposed at a red heat. It combines readily with oxygen, producing reddish-brown fumes, which dissolve in water, and probably consist in part of nitrous anhydride N_2O_3 and partly of nitrogen peroxide NO_2. When mixed with water-vapour it is converted into nitric acid and oxygen under the influence of a succession of electric sparks. Nitric oxide extinguishes the flame of a taper, and it gives up its oxygen only when heated to a high temperature with readily oxidisable substances, such as phosphorus.

Preparation.—Nitric oxide is prepared by the action of copper or mercury on nitric acid diluted with an equal bulk of water and without the aid of heat,

$$8HNO_3 + 3Cu = 3(Cu\,2NO_3) + 2NO + 4H_2O,$$

or by decomposing potassium nitrate by dilute sulphuric acid in the presence of ferrous sulphate,

$$2KNO_3 + 6FeSO_4 + 5H_2SO_4 = 2HKSO_4 + 3Fe_2\,3(SO_4) + 4H_2O + 2NO.$$

NITROUS ANHYDRIDE.

FORMULA N_2O_3. MOLECULAR WEIGHT 76.

Composition.—This substance contains rather more than six-tenths of its weight of oxygen, the nitrogen being combined with one and a half times its volume of oxygen.

Characters.—Nitrous anhydride is a reddish-coloured gas, that condenses to a blue liquid at $-18°$.

Preparation.—By gently heating a mixture of nitric acid and arsenous oxide, or a mixture of starch and nitric acid of 1·25 sp. gr., brown vapours are given off which may be condensed in a tube surrounded by a freezing mixture to a blue liquid, after having been passed over calcium chloride. The reaction that takes place is represented by the following equation:

$$As_2O_3 + 2HNO_3 + H_2O = 2H_3AsO_4 + N_2O_3.$$

Compounds.—Nitrous anhydride combines with water forming nitrous acid HNO_2, the representative of a series of saline compounds called nitrites.

It is a very unstable compound, and is readily decomposed into nitric acid, nitric oxide, and water, as shown by the following equation:

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

The nitrites are generally crystallisable and soluble in water, the silver and lead salts being the least soluble; when heated they melt, and on raising the temperature they are decomposed, giving off a mixture of oxygen and nitrogen. An acidulated solution of a nitrate acts both as a reducing and as an oxidising agent. Permanganic acid is at once reduced in this way, as well as chromic acid, salts of gold and mercury, etc. On the contrary, iodine is liberated from potassium iodide by an acidulated solution of a nitrite, ferrous salts are converted into ferric salts, and indigo is bleached by oxidation. Nitrites frequently occur in water contaminated by surface drainage.

NITROGEN PEROXIDE.

FORMULA NO_2 OR N_2O_4. MOLECULAR WEIGHT ~~23 OR~~ 46. or 92

Composition.—This substance contains nearly seven-tenths of its weight of oxygen, the nitrogen being combined with twice its volume of oxygen, and the joint volume of the constituent gases is condensed to one-third by their combination.

Characters.—At the ordinary temperature nitrogen peroxide is an orange-coloured liquid, having a specific gravity of 1·45. When cooled, the colour fades and it becomes greenish or even quite colourless, and at a very low temperature it crystallises. It boils at 22°, giving off reddish-brown vapour, which becomes darker-coloured when heated somewhat above that temperature, and at 40° almost black. The density of the gas as compared with hydrogen is 38·3 at 26·7°, but at 135° it is only 23.

Nitrogen peroxide is decomposed by water, forming nitrous acid and nitric acid, as shown by the following equation:

$$2NO_2 + H_2O = HNO_2 + HNO_3.$$

When liquid nitrogen peroxide is gradually mixed with water the liquid becomes blue, then green, and lastly orange-coloured, nitric oxide being evolved and nitric acid formed,

$$3NO_2H_2O = NO + 2HNO_3.$$

Nitrogen peroxide is decomposed by basic oxides, such as potash, forming nitrate and nitrite,

$$2NO_2 + 2KHO = KNO_2 + KNO_3 + H_2O.$$

The gas has a suffocating odour; it does not extinguish the flame of a taper; it is not decomposed at a moderate red-heat; but heated phosphorus or carbon abstract oxygen from it—potassium does the same at the ordinary temperature.

Preparation.—By heating dry lead nitrate in a glass retort or flask, dark-red vapour is given off, consisting of a mixture of the peroxide with oxygen gas; and by passing the dry vapour through a cooled tube the peroxide is condensed. The reaction is represented by the following equation:

$$2(Pb\,2NO_3) = 2Pb\,O + 4NO_2 + 2O.$$

Compounds.—Nitrogen peroxide does not form saline compounds; but it combines with sulphuric acid, forming a crystalline substance.

NITROGEN PENTOXIDE.

FORMULA N_2O_5. MOLECULAR WEIGHT 108.

Composition.—This substance contains nearly three-fourths of its weight of oxygen, and it is very unstable, decomposing gradually at the ordinary temperature.

Characters.—Nitrogen pentoxide is colourless and crystalline, melts at 30°, and boils at 45°. It has a powerful action on oxidisable substances, such as sulphur, phosphorus, etc.

Preparation.—By passing dry chlorine gas over dry crystals of silver nitrate heated to about 90°, and lowering the temperature when decomposition commences, a compound of nitric peroxide and chlorine is formed, as shown by the following equation:

$$AgNO_3 + Cl = AgCl + NO_2Cl + O.$$

This substance then acts upon the undecomposed silver nitrate, forming nitrogen pentoxide.

$$NO_2Cl + AgNO_3 = AgCl + N_2O_5.$$

Compounds.—Nitrogen pentoxide combines with water, forming hydrogen nitrate or nitric acid, which is the representative of a series of saline compounds called nitrates.

$$\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O = 2\left\{\begin{matrix}NO_2\\H\end{matrix}\right\}O.$$

The nitrates are mostly soluble crystallisable salts; some few are decomposed by water into basic salts that are insoluble or sparingly soluble in water. By heat nitrates are readily decomposed, either giving off oxygen and being converted into nitrites, as in the case of the potassium salts, or yielding nitrogen peroxide and oxygen, as in the case of lead nitrate. Other nitrates, like bismuth and aluminum nitrates, give off nitric acid even when moderately heated.

When nitrates are heated with oxidisable substances in the dry state, they deflagrate or are decomposed with explosive violence, and their oxygen is transferred to the substance mixed with them: thus, for instance, carbon is converted into carbon dioxide, sulphur into sulphuric oxide, and these acid oxides combine with the basic oxide of the nitrate used, forming carbonate or sulphate.

Nitrates occur abundantly in the soil of some parts of India and South America, and they are formed by the gradual oxidation of nitrogenous organic substances in contact with chalk, limestone, or other earthy materials capable of forming bases. The potassium, sodium, and calcium salts are the most abundant. Magnesium nitrate sometimes occurs in water.

NITRIC ACID.

FORMULA HNO_3. MOLECULAR WEIGHT 63.

History.—The first description of the preparation of nitric acid was given by the Arabian chemist Geber, towards the end of the eighth century. He called it generally *aqua dissolutiva*, and sometimes *aqua fortis*. Glauber was the first to give it the name *spiritus acidus nitri*, which appellation was changed in the eighteenth century to *acidum nitricum* and nitric acid.

The characters of nitric acid were studied by Geber, and afterwards by Boyle, Mayer, Bergmann, and others. The knowledge of its composition is due to Cavendish, who in 1784 prepared nitric acid by the direct combination of nitrogen and oxygen by means of the electric spark.

The first directions for preparing nitric acid on a large scale, by distilling a mixture of clay and saltpetre, were given by Raymond Lully in the thirteenth century.

Occurrence.—Nitric acid does not occur to any extent naturally in the free state. Since it is a very strong acid, it expels weaker acids from their compounds and forms nitrates. The nitrates most often met with are those of potassium, sodium, calcium, and magnesium. Small quantities of ammonium nitrate are always present in the air, this salt being formed partly during thunderstorms, by the action of lightning upon the nitrogen, oxygen, and water of the air, and partly by the gradual oxidation of ammonium nitrite, small quantities of which are formed by the burning of most nitrogenous organic substances.

Composition.—In its most concentrated form, nitric acid, or hydric nitrate, contains more than three-fourths its weight of oxygen; its constitution is represented in accordance with the water type, by the formula $\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$.

Characters.—Nitric acid is an extremely corrosive liquid, fuming in the air, and possessing an irritating smell. When pure, it is colourless; but it assumes a yellow colour very quickly when exposed to the light, owing to the formation of nitrogen peroxide. When mixed with water this decomposition does not take place so readily. At a temperature of −50° nitric acid becomes solid; it boils at 86°, but does not distil without partial decomposition. When passed through a porcelain tube heated to redness, nitric acid is for the greater part decomposed into nitrogen peroxide, oxygen, and water; at a still higher temperature nitrogen is liberated, and some nitric oxide is formed. Nitric acid at 0° has a specific gravity of 1·559; at 15° a specific gravity of 1·530. The specific gravity of an aqueous solution of the acid decreases with the amount of water, hence it is easy to determine the relative strength of solutions of nitric acid from their specific gravity. The following table shows the percentage of nitric anhydride and nitric acid monohydrate in solutions of nitric acid of different specific gravities at a temperature of 15°.

Specific Gravity	Nitric Monohydrate	Nitric Anhydride	Specific Gravity	Nitric Monohydrate	Nitric Anhydride
1·530	100·00	85·71	1·368	58·88	50·47
1·529	99·52	85·30	1·363	58·00	49·71
1·523	97·89	83·90	1·358	57·00	48·86
1·520	97·00	83·14	1·353	56·10	48·08
1·516	96·00	82·28	1·346	55·00	47·14
1·514	95·27	81·66	1·341	54·00	46·29
1·509	94·00	80·57	1·339	53·81	46·12
1·506	93·01	79·79	1·335	53·00	45·40
1·503	92·00	78·85	1·331	52·33	44·55
1·499	91·00	78·00	1·323	50·99	43·70
1·495	90·00	77·15	1·317	49·97	42·83
1·494	89·56	76·77	1·312	49·00	42·00
1·488	88·00	75·43	1·304	48·00	41·14
1·486	87·45	74·59	1·298	47·18	40·44
1·482	86·17	73·86	1·295	46·64	39·97
1·478	85·00	72·86	1·284	45·00	38·57
1·474	84·00	72·00	1·274	43·53	37·31
1·470	83·00	71·14	1·264	42·00	36·00
1·467	82·00	70·28	1·257	41·00	35·14
1·463	80·96	69·39	1·251	40·00	34·28
1·460	80 00	68·57	1·244	39·00	33·43
1·456	79·00	67·71	1 237	37·95	32 53
1·451	77·66	66·56	1·225	36·00	30·89
1·445	76·00	65·14	1·218	35·00	29·29
1·442	75·00	64·28	1·211	33·86	29·02
1·438	74·01	63·44	1·198	32·00	27·43
1·435	73·00	62·57	1·192	31·00	26·57
1·432	72·39	62·05	1·185	30·00	25·71
1·429	71·24	61·06	1·179	29·00	24·85
1·423	69·96	60·00	1·172	28·00	24·00
1·419	69·20	59·31	1·166	27·00	23·14
1·414	68·00	58·29	1·157	25·71	22·04
1·410	67·00	57·43	1·138	23·00	19·71
1·405	66·00	56·57	1·120	20·00	17·14
1·400	65·07	55 77	1·105	17·47	14·97
1·395	64·00	54·85	1·089	15·00	12·85
1·393	63·59	54·50	1·077	13·00	11·14
1·386	62·00	53·14	1·067	11·41	9·77
1·381	61·21	52·46	1·045	7·22	6·62
1·374	60·00	51·43	1·022	4 00	3·42
1·372	59·59	51·08	1·010	2·00	1·71

The following table shows the percentage of nitric monohydrate and nitric anhydride in nitric acid solutions of different degrees Baumé, and at a temperature of 15°.

Degrees Baumé	Nitric Monohydrate	Nitric Anhydride	Degrees Baumé	Nitric Monohydrate	Nitric Anhydride
0	0·2	0·1	26	35·5	30·4
1	1·5	1·3	27	37·0	31·7
2	2·6	2·2	28	38·6	33·1
3	4·0	3·4	29	40·2	34·5
4	5·1	4·4	30	41·5	35·6
5	6·3	5·4	31	43·5	37·3
6	7·6	6·5	32	45·0	38·6
7	9·0	7·7	33	47·1	40·4
8	10·2	8·7	34	48·6	41·7
9	11·4	9·8	35	50·7	43·5
10	12·7	10·9	36	52·9	45·3
11	14·0	12·0	37	55·0	47·1
12	15·3	13·1	38	57·3	49·1
13	16·8	14·4	39	59·6	51·1
14	18·0	15·4	40	61·7	52·9
15	19·4	16·6	41	64·5	55·3
16	20·8	17·8	42	67·5	57·9
17	22·2	19 0	43	70·6	60·5
18	23·6	20·2	44	74·4	63·8
19	24·9	21·3	45	78·4	67·2
20	26·3	22·5	46	83·0	71·1
21	27·8	23·8	47	87·1	74·7
22	29·2	25·0	48	92·6	79·4
23	30·7	26·3	49	96·0	82·3
24	32·1	27·5	49·5	98·0	84·0
25	33·8	28·9	49·5	100·0	85·7

When nitric monohydrate is mixed with water, heat is set free, and the mixture thus obtained has a higher boiling point than the pure monohydrate. Upon distilling a mixture of nitric monohydrate and water, in which the proportion of water is relatively small compared with the acid, a stronger acid passes over at first, and there remains behind a more dilute acid, the boiling point of which remains constant at 123°. On the other hand, if a mixture of nitric acid with much water be distilled, the first portions of the distillate consist of nearly pure water, concentrated acid remaining behind in the retort. Upon continuing the distillation, the boiling point rises to 123°, and then remains constant, as in the former case. The acid which thus distils over has a specific gravity of 1·42, and has a composition corresponding to the formula ($2HNO_3,3H_2O$). This applies, however, only to a distillation under the ordinary pressure, change of pressure influencing the composition of the distillate.

The most important property of nitric acid is the oxidising action which it exerts in virtue of its capacity of yielding up to other bodies a portion of its oxygen. Thus, nitric acid easily oxidises carbon to carbonic acid, sulphur and sulphurous acid to sulphuric acid, and the metals to oxides, etc. The extensive application of nitric acid to industrial purposes is chiefly owing to its oxidising property.

Another important property of nitric acid is its nitrifying action, *i.e.*, its property of replacing the hydrogen of certain organic compounds by NO_2. An example of the kind is found in the case of the preparation of gun-cotton, formed by treating cotton (cellulose) with strong nitric acid:

$$C_6H_{10}O_5 + 3\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O = C_6H_7(NO_2)_3O_5 + 3H_2O.$$

Testing of Nitric Acid.—The strength of nitric acid is ascertained from its specific gravity. It is also necessary to test nitric acid for certain impurities with which it is always liable to be contaminated. Thus a yellowish colour may be due either to the presence of nitrogen peroxide or to the presence of compounds of chlorine or iodine. The presence of nitrogen peroxide is detected by dropping into a small quantity of the acid, in a test-glass, a few drops of a solution of potassium permanganate, the colour of which is discharged if nitrogen peroxide be present. Chlorine is found by diluting a small quantity of the acid, and adding a drop of a solution of silver nitrate, which gives a curdy precipitate if chlorine be present. Free iodine is detected with

starch paste, or by shaking the diluted acid with carbon bisulphide, which assumes a red tint if free iodine be present. Sulphuric acid is detected by diluting the nitric acid very considerably with water, and then adding a small quantity of a solution of barium nitrate, a white precipitate indicating the presence of sulphuric acid. Further, nitric acid ought not to leave a residue when evaporated upon a watch-glass or on platinum foil; a residue in such case would indicate the presence of substances, such as sodium sulphate, with which nitric acid may be contaminated by the spirting of the materials in the process of distillation.

Preparation.—Nitric acid is prepared on a small scale by distilling a mixture of equal parts of saltpetre and sulphuric acid in a retort. The following equation represents the change that takes place:

$$\begin{matrix}NO_2\\K\end{matrix}\Big\}O + \begin{matrix}SO_2\\H_2\end{matrix}\Big\}O_2 = \begin{matrix}SO_2\\KH\end{matrix}\Big\}O_2 + \begin{matrix}NO_2\\H\end{matrix}\Big\}O.$$

On the large scale the same materials are used, but Chili saltpetre (sodium nitrate) is generally substituted for potassium nitrate, the proportions in which these materials are used being 116 parts of Chili saltpetre to 100 parts of sulphuric acid. When a weaker acid is required, sulphuric acid of sp. gr. 1·551 is used, but the quantity taken must be larger in proportion to the degree of dilution.

Distillation of Nitric Acid.—In the distillation of nitric acid. gallery furnaces are often employed, in which a number of glass retorts charged with the mixture of saltpetre and sulphuric acid are heated in sand baths, the distillate being collected in spacious receivers of glass.

According to another process, the apparatus represented by fig. 12 is used. C is a retort of cast iron about four feet in diameter and three feet deep, with an opening above for admitting the mixture of saltpetre and sulphuric acid. This opening is

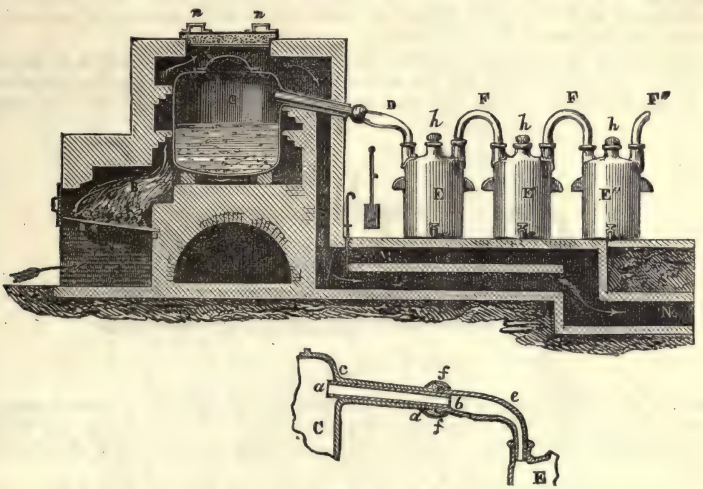


FIG. 12.

closed with a lid, luted on with clay and gypsum. The furnace is also closed with a lid (*n n*). The retort is connected with the receivers by means of an iron tube lined with clay, and a glass adapter (D). The condensers consist of a number of stoneware bottles (E, E′, E″, etc.), connected with one another by means of stoneware tubes (F, F′, F″, etc.) Each of these bottles holds from forty to fifty gallons, and is furnished with a cock below for running off the acid, as well as with an opening above closed by a stopper, through which the height of the acid in the jar may be ascertained, or water poured in. A condensing arrangement of this kind consists of ten or twelve bottles, the first few of which are left empty, while the last ones of the series contain a small quantity of water for the complete absorption of the nitric acid vapours. The retort is heated by means of the furnace (B), the heated air surrounding the retort on all sides, and escaping through the flue L N. At the beginning of the process the damper at the further end of the flue is so placed that the hot air is compelled to pass through the flue M. This is done so as to warm the first few stone receivers, whereby the risk of their cracking when the hot nitric vapours are admitted is avoided. As soon

as the nitric acid in the first few bottles has attained a height of from three to five inches, the damper is so placed that the hot air escapes through the flue L. If concentrated sulphuric acid has been employed, the first products of distillation are of a reddish brown colour, owing to the great excess of sulphuric acid at the beginning of the operation decomposing a portion of the nitric acid into nitrogen peroxide, oxygen, and water. In proportion, however, as the sulphuric acid is saturated by its action upon the saltpetre, the red vapours gradually disappear, until towards the end of the process, when they are again produced, owing to a decomposition that will be described when treating of fuming nitric acid (p. 48). It is easy to judge of the progress of the distillation by observing the colour of the vapours passing through the glass tube (D).

Formerly, and even now in some places, the distillation was conducted in cast-iron retorts placed in a horizontal position, and furnished above with a lining of fire-bricks as a protection against the acid vapours. Two such retorts are heated by a single furnace, the condensation being effected by an arrangement similar to that shown in fig. 12.

At the end of the operation the residue in the retort, after cooling, contracts, and is taken out. When ordinary saltpetre has been used, it is worked for potassium sulphate, or when Chili saltpetre has been employed, for neutral sodium sulphate. The residue can also be employed in the preparation of fuming sulphuric acid. In order to save time when retorts are used, the residue may be removed without waiting until it has cooled. To effect this, it is only necessary to furnish the lid of the retort at its lowest point with a small opening closed with a stopper or plug, which is cemented in with a luting of clay during the heating. Upon removal of the stopper directly the distillation is over, the molten residue flows out, and the retort can be charged again immediately.

The preparation of nitric acid as well as soda from Chili saltpetre may be effected, according to M. Walz, by mixing the saltpetre intimately with chalk, and heating such mixture in a retort, in a current of steam, when nitric acid distils over, and is collected in receivers of the usual form.

Bleaching of Nitric Acid.—The crude distillate is always coloured yellow by nitrogen peroxide. To remove this the raw acid is heated in vessels having the form shown in fig. 13, placed in a water bath that can be heated to 80° or 85°, until no further

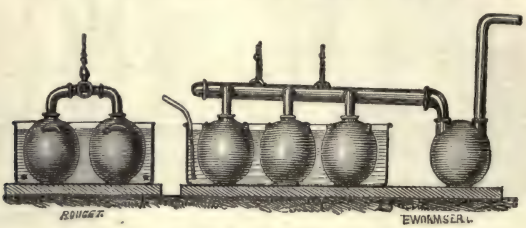


Fig. 13.

evolution of coloured vapour is observed. The vapour escaping is passed through a tube into a cool carboy, where a small quantity of liquid acid collects, and finally it is discharged into the air, or into lead chambers for the production of sulphuric acid.

Direct Preparation of Bleached Acid.—Since brown vapours are formed only at the

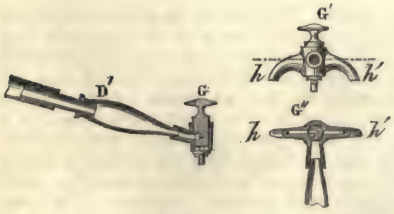


Fig. 14.



Fig. 15.

beginning and end of the process, it is possible to separate such coloured products from the colourless portion by a simple fractional distillation. For this purpose the

glass adapter (D, fig. 14) through which the vapours escape from the distilling vessel, is connected with a stoneware cock (G) so constructed that by turning the cock (G) the vapours pass either through *h* or *h'*, and are conducted into different receivers, one serving for the coloured and the other for the colourless products. The same end is attained by the arrangement shown by fig. 15. One of the limbs of a three-limbed lute (K K') fits over the end of the glass adapter of the distilling vessel, and admits of being turned so that the two other limbs are respectively raised or lowered, and the vapours passing through them passed into one or other of two receivers, one of which receives the coloured, the other the colourless vapours. During the time that the one limb of the lute (K K') is lowered and placed in connection with the receiver, the other end is closed with a glass plug. By the use of either of the above arrangements an acid may be obtained which can be sent direct into the market.

Improved Condensing Apparatus of MM. Devers and Plisson.—This is shown in fig. 18. A is a glass adapter, through which the nitric acid vapours from the generators (in this case cast-iron retorts) escape. The end of the adapter is luted air-tight into the tubulus of the carboy (B), which rests upon a flue, serving to heat it. The acid which condenses in B flows through a syphon (*d*, fig. 16), the outer limb of which is shorter than the inner, thus preventing the complete emptying of the carboy, and forming an hydraulic joint. From B the acid flows into another vessel (B) beneath it. The carboys (C E F H) have the same construction as B, and the acid condensed in them flows through the syphons into a stoneware tube, and finally collects in a receiver (O). The upper part of the carboy (B) is furnished with a funnel of the form shown in fig. 17, which admits of water being poured into the carboy. Conical-shaped vessels (D D G G), having an aperture at their lower extremity, and furnished

Fig. 16.



Fig. 1 .



Fig. 18.

above with funnels (P P) of the same construction as that shown in fig. 17, fit into the necks of the carboys (C E F H). The vapours from B pass through a stoneware tube into the second carboy C, and from thence into D, placed above C, through D E F G G H.

The vapours are thereby compelled to traverse a long distance, which secures their complete condensation. The condensed acid flows from the upper vessels D D G G into the lower ones C E F H, and from thence into the receiver O. The concentration, as well as the condensation, of the acid may be regulated by pouring small quantities of water or very dilute acid, at intervals, through the funnels P P. The uncondensed vapour passes from the last carboy H into the three carboys I I′ I″, filled with pieces of moist pumice and placed one above another. For the condensation of the last traces of vapour, it can be passed from the carboy I″ into a stoneware worm condenser J, through which a current of cold water is allowed to flow downwards from the cock M, passing over the pieces of pumice, which it keeps constantly moist. The moist pumice favours the action of oxygen upon the vapour of nitrogen peroxide, formed at the beginning and end of the operation, and causes its reconversion into nitric acid, which collects in the vessel N below.

This condensing apparatus has the great advantage that it requires emptying and reconstruction much less frequently (every two or four weeks), and thereby saves labour. At the same time the consumption of luting is considerably less, and the vapours are more thoroughly condensed than in any other form of apparatus at present employed.

The amount of acid obtained by the use of this apparatus is 120 or 130 parts, containing 50 per cent. of nitric monohydrate for every 100 parts of Chili saltpetre.

The complete purification of nitric acid from unavoidable admixture of sodium sulphate, chlorine, etc., is effected by submitting it to a further distillation, one or two per cent. of lead nitrate being previously mixed with the acid to effect the retention of both impurities.

Fuming Nitric Acid.—When a mixture of saltpetre and sulphuric acid in equivalent proportions is distilled, the distillate does not consist of an acid so pure as that obtained by distilling the saltpetre with two equivalents of sulphuric acid, but is a mixture of nitrogen peroxide and nitric acid, which bears the name of fuming nitric acid. The formation of the large quantities of nitrogen peroxide depends upon the fact that in the first stage of the process acid potassium sulphate and nitric monohydrate are formed (vide p. 45). When the temperature is raised to 220°, the acid potassium sulphate is decomposed into neutral potassium sulphate and sulphuric acid, which acts upon the saltpetre present in the retort. The nitric acid thus set free is partly decomposed at this elevated temperature into oxygen and nitrogen peroxide, which passes over with the distillate, and is absorbed by the nitric acid.

Red fuming nitric acid must therefore be considered as a mixture of nitric acid and nitrogen peroxide. It is extremely corrosive and exerts a very energetic oxidising action. When slightly heated it gives off nitrogen peroxide, a reaction which serves for the preparation in the pure state of this substance. Upon gradually mixing red fuming nitric acid with water, its colour passes through various shades from reddish yellow to green and blue, and when enough water has been added, it finally becomes colourless. These changes of colour are due to the transitory formation of blue nitrous acid by the action of water upon nitrogen peroxide. At the same time red vapours escape which owe their origin in part to the oxidising action of the air upon nitric oxide formed by the reaction, and in part either to the direct formation of nitrous acid or to the evaporation of nitrogen peroxide.

Brunner's method of preparing red fuming nitric acid consists in distilling saltpetre with an equal weight of sulphuric acid and 3½ per cent. of starch, which decomposes some nitric acid and produces nitrogen peroxide.

Uses.—Nitric acid owes its large consumption partly to its powerful oxidising and dissolving action, and partly to its nitrifying properties. It is extensively used in the preparation of sulphuric acid, in preparing chemically pure phosphoric acid from phosphorus, also in preparing iodic and arsenic acids. It is used for etching bronze, brass, and copper, for separating gold from silver; further, by engravers for etching copper plates; in the preparation of aqua regia, the latter serving as a solvent for gold, platinum, etc. Nitric acid is also employed in the preparation of various nitrates, such as silver (lunar caustic of the surgeon), mercury, copper, and lead nitrates; in the preparation of tin chloride, the neutral and basic nitrates of bismuth; in the manufacture of pure oxalic acid, gun-cotton, nitroglycerine, and nitrobenzol, the substance from which aniline colours are prepared; nitric acid is also used in the preparation of anthraquinone, from which artificial alizarine is obtained; in the preparation of phthalic acid, nitromannite, Martin's yellow, and picric acid. Nitric acid is further used for colouring silk, wool, and other animal substances, for the conversion of starch into dextrin, for the decomposition of indigo in cotton-printing, for preparing iron liquor (rouille) used for colouring silk black, etc.

Aqua Regia, or nitro-muriatic acid, is prepared by mixing nitric acid with four times its volume of hydrochloric acid. It is a solvent for a number of metals, such as gold, iridium, platinum, etc., which are not attacked by the strongest acids. The action of this mixture is due to the presence of free chlorine, which is liberated on heating,

$$HNO_3 + 3HCl = NO + 2H_2O + 3Cl.$$

The liberated chlorine combines with the metal to be dissolved, forming with it a chloride.

Under certain conditions aqua regia exerts an oxidising action; thus by its means sulphur is oxidised to sulphuric acid, arsenic to arsenic acid, etc.

Upon heating aqua regia and collecting the vapours evolved, the first product which distils over consists of nitric oxydichloride, $NOCl_2$, a substance boiling at 7°, and afterwards a product passes into the receiver having a composition represented by the formula NOCl, and termed nitrous oxychloride.

AMMONIA.

FORMULA NH_3. MOLECULAR WEIGHT 17.

History.—This substance was certainly known as early as the thirteenth century, a solution of it having been prepared from urine by Raymond Lully. A similar solution has long been known under the name of spirits of hartshorn. The capability of forming saline compounds with acid, which constitutes the analogy between ammonia and the mineral alkalies, was also known to the ancient chemists. In the gaseous state ammonia was first obtained and described under the name of alkaline air by Priestley in 1774. Bergman gave it the name ammonia in 1782 on account of its having been obtained from *sal ammoniac*, which was prepared by the distillation of camels' dung near the temple of Jupiter Ammon in Egypt. The composition of ammonia was ascertained by Berthollet in 1785.

Occurrence.—Ammonia does not occur naturally in the free state. Combined with carbonic acid, and sometimes with nitrous or nitric acids, it exists, in small proportion, in the atmosphere. It is also met with, probably in the state of chloride, in sea water, and in the water of many springs. In volcanic districts ammonia occurs abundantly in the state of chloride, and considerable quantities of the carbonate are sometimes found in deposits of guano. At the present time, however, the chief source of ammonia is the gas liquor obtained in the distillation of coal for the preparation of illuminating gas. In all cases of the decomposition of carbonaceous materials containing nitrogen, either by putrefaction or destructive distillation, ammonia is found among the products.

The presence of a small proportion of ammonia in the atmosphere is of great importance for agriculture, since ammonia is essential for the nutrition of plants, and owing to its solubility it is washed out by dew, rain, etc., falling on the earth's surface. The ammonia in the air is generally combined with nitrous acid, which is formed in considerable quantities during thunderstorms by the electric discharges. Whether the ammonia in the air is also itself produced in part by electricity, or whether the ammonium nitrite is formed by the combination of already existing ammonia with nitrous acid, is not determined. At any rate, a number of chemical processes taking place upon the earth give rise to the formation of considerable quantities of ammonia, as, for instance, the putrefaction of nitrogenous organic materials such as animal remains. Traces of ammonia are also contained in the air exhaled from the lungs of animals.

Composition.—Ammonia contains rather more than four-fifths of its weight of nitrogen, and nearly one-fifth its weight of hydrogen. The hydrogen it contains has, in the free state, a normal volume three times that of the nitrogen.

Characters.—Ammonia is gaseous at the ordinary temperature: and therefore it is represented as a compound of three atomic proportions of hydrogen with one atomic proportion of nitrogen, and the joint volume of its constituents in the free state is condensed to one half; its density is 8·5 times that of hydrogen. Its specific gravity (air = 1) is 0·5893. It can be converted into the liquid state either by the application of a pressure of from 6 to 7 atmospheres, or by cooling to a temperature of −40°. At a temperature of −80° it assumes a crystalline condition. Ammonia gas is colourless: it possesses an extremely penetrating smell, and excites a copious flow of tears. When an electric current is passed through the gas, it is decomposed into its constituents. It is decomposed in the same way when passed through a porcelain tube heated to

redness. This decomposition takes place more readily if the tube be filled with pieces of porcelain, and easiest of all if pieces of platinum, silver, iron, or copper, be placed in the tube.

If ammonia gas be conducted by means of a narrow tube into an atmosphere of oxygen, it may be inflamed by the application of a light, and will continue to burn. It is not, however, capable of burning in atmospheric air, except when kept continually in contact with a flame of some other more combustible substance. Ammonia is extremely soluble in water, which at a temperature of 0°, and under a pressure of 760 mm., dissolves 1,500 times its volume of the gas. The liquid ammonia of commerce is a solution of the gas in water. Water absorbs ammonia with such energy that it rushes into a space filled with ammonia just as it would into a vacuum, and a tube may often be shattered in this way. At higher temperatures, the solubility of ammonia in water is very much less, water at 15° C. absorbing only 727 times its volume of ammonia, and at a temperature of 25° only 586 times its volume. In the absorption of ammonia gas by water there is a considerable increase in the volume, and a corresponding reduction in the density of the liquid. Therefore, specific gravity affords a ready means of determining the ammoniacal contents of the solution, as shown by the following table.

TABLE SHOWING THE AMOUNT OF AMMONIA IN SOLUTIONS OF AMMONIA. TEMPERATURE 14° (Carius.)

Ammonia in 100 parts solution	Specific Gravity	Ammonia in 100 parts solution	Specific Gravity	Ammonia in 100 parts solution	Specific Gravity	Ammonia in 100 parts solution	Specific Gravity
1	·9959	10	·9593	19	·9283	28	·9026
2	·9915	11	·9556	20	·9251	29	·9001
3	·9873	12	·9520	21	·9221	30	·8976
4	·9831	13	·9484	22	·9191	31	·8953
5	·9790	14	·9449	23	·9162	32	·8929
6	·9749	15	·9414	24	·9133	33	·8907
7	·9709	16	·9380	25	·9106	34	·8885
8	·9670	17	·9347	26	·9078	35	·8864
9	·9631	18	·9314	27	·9052	36	·8844

Aqueous solutions of ammonia occur in commerce under various appellations, such as solution of ammonia, liquid ammonia, spirits of hartshorn, etc.

Ammonia combines with hydrochloric acid, forming solid sal ammoniac; hence arise the white fumes observed when an open vessel containing ammonia is brought into the vicinity of one containing hydrochloric acid. This property of ammonia is made use of for ascertaining its presence. A glass rod is moistened with hydrochloric acid, and held over the liquid that is to be tested for ammonia. If a fume of sal ammoniac is formed, the presence of ammonia is proved.

Preparation.—Ammonia is prepared from its saline compounds, principally from the sulphate or chloride. The salts of ammonia, as well as free ammonia, are obtained as by-products of the manufacture of illuminating gas, or by the destructive distillation of nitrogenous organic substances, such as animal refuse, old leather, blood, etc., and in Egypt from camel's dung.

For the preparation of ammonia on a small scale, finely-powdered sal ammoniac is mixed with freshly slaked lime, and the mixture introduced into an iron retort. The neck of the retort is connected with a Woulfe's washbottle containing a very small quantity of water, so that the ammonia gas produced upon heating the retort may be washed free from any solid particles carried over mechanically. If it be desired to use the gas in a dry state, it must then be passed through a U-tube filled with pieces of fused potassium hydrate and collected over mercury.

When ammonia has to be prepared on a large scale, a large iron still is employed upon which a head is fixed air-tight by means of luting and screws. The head is connected with a condenser delivering into a glass flask. A delivery tube is fitted with a cork into the neck of the flask and made to dip into a vessel two-thirds filled with pure water. The still is charged with 100 pounds of sal ammoniac or ammonium sulphate, and an equal weight of fresh-burnt lime, previously mixed with four times its weight of water, the whole being mixed together by stirring. The head is then luted and screwed down air-tight upon the still, and heat is applied, gently at first,

the temperature being gradually raised. The process that takes place is represented by the following equation:—

$$\left.\begin{matrix}Ca\\H_2\end{matrix}\right\}O_2 + 2\left\{\begin{matrix}NH_4\\Cl\end{matrix}\right. = \left.\begin{matrix}Ca\\Cl_2\end{matrix}\right\} + 2\left\{\begin{matrix}H\\H\end{matrix}\right\}O + 2NH_3.$$

Together with ammonia gas, aqueous vapour is also given off, but this condenses in the cooling apparatus, and collects in the flask, while the ammonia passes into the water of the second vessel, where it is absorbed. Since the solution of ammonia produced is lighter than water, and therefore rises to the surface, the delivery tube is made to terminate in the lowest part of the absorption vessel.

Uses.—Ammonia is much employed in medicine. Its use for this purpose is owing to its strong caustic action, producing blisters when applied to the skin, to its action upon the sensorium, acting in cases of syncope as a restoring agent, and to its strong basic properties. Advantage is taken of this property for neutralising the carbonic acid and sulphuretted hydrogen which are formed in a certain disease of the herbivora, in consequence of over-feeding with green food. Ammonia is further extensively used in chemical laboratories for all sorts of purposes, both in analysis and in the manufacture of preparations. Its use in this way is generally owing to its strong basic properties, rendering it possible to neutralise by its means the strongest acids, and to precipitate nearly all the oxides of the metals in a solid condition from solutions of their salts. It is further employed on a large scale in cotton-printing, in bleaching, and for the preparation of lakes and colours.

Compounds.—Ammonia forms numerous compounds with hydracids and with the hydrogen salts of acid oxides. These compounds are termed *ammoniacal salts*, and they correspond closely with the potassium and sodium salts of acid oxides, but contain, instead of the metals potassium or sodium, a compound molecule NH_4 which takes their place as a pseudo-metal, and is termed *ammonium*. Thus, for instance, the compounds of ammonia with hydrochloric acid and with nitric or sulphuric acid can be represented by the formulæ:

NH_3HCl	or	NH_4Cl	corresponding to	KCl
NH_3HNO_3	or	NH_4NO_3	„ „	KNO_3
$2(NH_3),H_2SO_4$	or	$2(NH_4),SO_4$	„ „	K_2SO_4

Ammonia also combines with many chlorides, nitrates, sulphates, and other salts, forming compounds which are probably so constituted that they contain compound molecules analogous to ammonium, with one or more atomic proportions of a metal in the place of part or the whole of the hydrogen of ammonium. Thus the compound NH_2HgCl, formed by the action of ammonia upon mercuric chloride, may be regarded as the chloride salt of mercurammonium, corresponding to ordinary ammonium chloride, but with two atomic proportions of hydrogen replaced by the divalent metal mercury.

AMMONIUM CHLORIDE.

Formula NH_4Cl. Molecular Weight 53·5.

History.—This substance, commonly known as *sal ammoniac*, was at one time obtained almost exclusively from Egypt, and was prepared by sublimation from the soot produced by burning camel's dung as fuel.

Occurrence.—Ammonium chloride occurs naturally in volcanic districts as an incrustation on the surfaces of fissures; also in sea water and in very small amount in the water of some springs.

Characters.—Ammonium chloride is a colourless translucent substance, crystallisable in octahedra, which are generally grouped together in arborescent forms. It sometimes occurs in the cubic form. The salt dissolves in about three times its weight of cold water, and in its own weight of boiling water; its solution in cold water is attended with considerable reduction of temperature. Ammonium chloride volatilises without melting.

Preparation.—Ammonium chloride is prepared by sublimation from a mixture of ammonium sulphate and sodium chloride or from the ammoniacal liquor of gas works, by neutralising it with hydrochloric acid, evaporating the solution until the salt crystallises, and then purifying by sublimation.

Uses.—Ammonium chloride is largely used for cleaning the surface of metals in tinning and soldering; also in the manufacture of alum, and for preparing freezing mixtures.

AMMONIUM SULPHATE.

FORMULA $2(NH_4),SO_4$. MOLECULAR WEIGHT 132

Occurrence.—Ammonium sulphate occurs naturally as a mineral called mascagnin in volcanic districts, also in the water of the Tuscan lagunes, and sometimes as an efflorescence on the surface of the earth.

Characters.—Ammonium sulphate forms colourless transparent prismatic crystals, isomorphous with potassium sulphate. It dissolves in twice its weight of cold water, and in its own weight of boiling water. It is hygroscopic; when heated it decrepitates, melts at 140°, and is decomposed at a higher temperature.

Preparation.—Ammonium sulphate is prepared from gas liquor, and from the ammoniacal liquor obtained in distilling bituminous shale, by neutralising with sulphuric acid or filtering the liquors through layers of gypsum, by which the carbonate of ammonia they contain is converted into sulphate; then evaporating and crystallising the salt.

Uses.—Ammonium sulphate is largely used as a manure.

AMMONIUM CARBONATES.

There are three definite ammonium carbonates: the neutral carbonate $2(NH_4),CO_3H_2O$, the acid carbonate NH_4HCO_3, commonly called bicarbonate, and the sesquicarbonate $4(NH_5),H_2\ 3(CO_3)$, called also volatile salt or salts of hartshorn.

The substance commonly met with as carbonate of ammonia, consists chiefly of the latter compound. It is a translucent fibrous mass, having a strong ammoniacal smell, and is obtained by sublimation from a mixture of ammonium sulphate and chalk.

PREPARATION OF AMMONIA FROM GAS LIQUOR.—The watery liquor obtained in the manufacture of gas from coal contains most of the nitrogen of the coal in the form of ammonia. Its composition varies according to the kind of coal employed, as shown by the following table of analyses by Gerlach:—

100 cub. cent. contain		grams.	grams.	grams.
Ammonium	Hyposulphite	·1036	0·1628	·5032
,,	Sulphide	·0340	·0646	·6222
,,	Carbonate $(NH_4)HCO_3$	·1050	·1470	·2450
,,	,, $2(NH_4),CO_3$	·4560	·7680	3·3120
,,	Sulphate	·0462	0·0858	0·1320
,,	Chloride	3·0495	1·7120	0·3745

Besides these salts, gas liquor contains some ammonium sulphocyanide and benzoate, and on the average it contains from 1 to 5 per cent. of ammonia.

The gas liquor is mixed with lime and subjected to distillation in a boiler (A, figs. 19 and 20) set over a furnace, the flue of which passes round a second boiler (B), containing a similar mixture of gas liquor and lime. The ammonia gas driven off by the

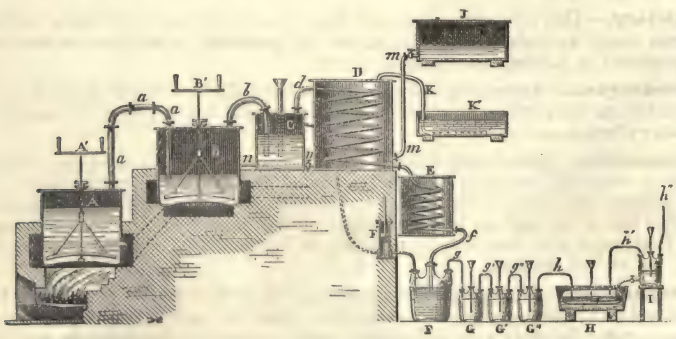


FIG. 19.

heat, passes through the tube (*a a*) into the second boiler (B), where it is washed, and then passes by the tube (*b*) into the washing vessels (C and C′), which are charged with milk of lime for the purpose of separating impurities from the ammonia. It then

passes through the worms of the condensers (D and E), and is thus to a great extent deprived of water-vapour. The gas is then passed through several smaller washing vessels (F G G′G″) into a leaden vessel (H) surrounded with cold water, and containing water for the absorption of the gas. The vessel I serves for condensing any ammonia that may escape from the leaden vessel (H), and its contents can from time to time be run into the leaden vessel.

The liquid condensing in the vessel F is raised by the pump (F′) into the washing vessel (C), and a stream of fresh gas liquor is occasionally run from a tank (J) into the condenser (D), so as to serve for cooling, and to become warmed before it is run into the washing vessel (C) on its way into the boilers (B and A). In order to save any

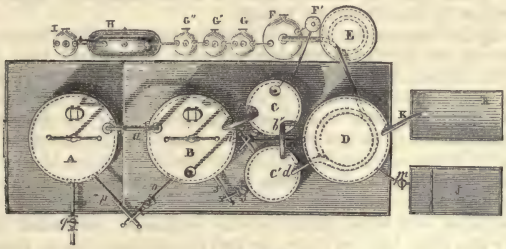


FIG. 20.

ammonia given off by the heating of the gas liquor thus passed through the condenser (D), this vessel is connected by means of a pipe (K) with a leaden tank (K′), containing sulphuric acid. When the whole of the ammonia has been expelled from the liquid in the boiler (A), the contents are drawn off, and the liquid already heated in the second boiler (B) is run into A, the boiler B being also charged again with heated gas liquor from D, and heated milk of lime from C and C′, and then the operation is continued as before.

Instead of using milk of lime for the purification of ammonia gas, freshly ignited charcoal is sometimes employed, and the gas is passed through closed iron cylinders filled either with that material or coke, which is kept moist with the refuse oil obtained in the distillation of tar or in the manufacture of paraffin oil. This plan has the advantage of separating the napthalin with which ammonia obtained from gas liquor is liable to be contaminated, and it also prevents the stoppage of the condensing worms by the napthalin carried over by the hot gas.

In order to prepare ammonium sulphate the ammonia gas is passed entirely into a lead-lined tank containing sulphuric acid of about 1·512 sp. gr. The sulphate separating in small crystals is raked out of the tank into strainers placed so that the liquor runs back into the tank, and when the salt is sufficiently drained it is dried. In proportion as the salt is removed fresh sulphuric acid is added, and the operation is continued in this way until the mother-liquor becomes charged with empyreumatic substances, oil, etc., when it is evaporated separately, and the tank charged with fresh sulphuric acid as before. The ammonia salt contains less oily impurity when the liquor in the tank is kept slightly acid.

Ammonium chloride is prepared in the same way by substituting hydrochloric acid for sulphuric acid, and passing the cooled ammonia gas into it. In order to obtain it pure, it must be recrystallised after the solution has been boiled with some nitric acid to destroy empyreumatic impurities.

THE ATMOSPHERE.

History.—Anaximenes, who flourished in the sixth century before Christ, regarded air as the principle or element out of which all other substances took their origin either by dilution or condensation. In the 'natural system' of Aristotle, also, air constituted one of his four elements—earth, air, fire, and water—and together with the belief in the four elements of Aristotle, the opinion that air was an elementary body held its ground until near the end of the eighteenth century.

Lavoisier was the first to point out that atmospheric air consists of several substances. His views upon the chemical nature of the atmosphere have not been materially altered by the numerous researches of later chemists.

Composition.—The atmosphere contains several different gases which are not, however, chemically combined with one another, but only mechanically mixed. The principal constituents are nitrogen and oxygen; beside these, atmospheric air contains appreciable quantities of water-vapour and carbonic acid. Nitric and nitrous

acids, ammonia, ozone, and hydrogen are also present in the air, but in such small proportions that their amount cannot well be determined with certainty. Air contains on an average, in 100 volumes:—

	By measure	By weight
Nitrogen	78·492	77
Oxygen	20·627	23
Water-vapour	0·840	
Carbonic acid	0·041	
	100·000	

Since these gases differ in density, there is a corresponding difference in their relative proportions by weight and by volume.

By comparing the composition of the air in the deepest valleys with the composition of the air on the highest mountain summits, it is found that the relations between nitrogen, oxygen, and carbonic acid remain the same, except under certain local influences, such as the proximity of active volcanoes emitting vast streams of carbonic acid, or extraordinarily luxuriant vegetation using up a large amount of carbonic acid, and producing on the other hand a great quantity of oxygen.

This constancy in the relative proportions of the constituents of atmospheric air is due to 'diffusion,' according to which gases intermix uniformly with each other, however much they may differ in density.

Modern researches have shown that there are contained suspended in the air in the form of very fine dust, besides inorganic and organic substances, minute organised particles which are recognisable under the microscope as spores and germs which upon contact with materials favourable to their nourishment are developed and form ferments. Thus yeast, or the ferment which causes alcoholic fermentation, is only produced when the liquid to be fermented comes into contact with the air, provided the liquid does not already contain the ferment. It is the same as regards lactic fermentation, and other processes of fermentation and putrefaction. How far the hypothesis is justified, that certain epidemic diseases, such as cholera, etc., are determined by the presence of germs or spores in the air, which, owing to a process similar to fermentation, bring about a diseased condition of the animal organism, cannot be here discussed.

Condition of the Atmosphere in Nature.—The atmosphere surrounding our planet as a gaseous envelope is retained in this position by the attraction of the earth, and consequently it partakes of the motion of the earth. As a result of the attraction of the atmosphere by the earth, the upper portion exerts a pressure upon the lower portion, and, since atmospheric air is compressible, the lower portion of the aërial envelope is therefore denser than the upper portion. The higher a mountain is ascended the smaller does the density of the air become. This is the reason why respiration is more difficult at great heights. The lungs require a certain quantity of air, and as the density of the air is less at great heights, a larger volume of such air is required than of the denser air of lower elevations; respiration must therefore be more rapid.

The atmosphere exerts pressure upon the entire surface of the earth. At the sea-level this pressure equals that exerted by a column of mercury 760 mm. in height (29·922 inches). The pressure upon each square decimetre is therefore 103·33 kilos, or nearly 15 lbs. upon the square inch.

At a height of 5,528 metres (18,136 feet) the atmospheric pressure amounts to only 7½ lbs. upon the square inch, or half of what it is at the level of the sea.

From the refraction of the rays of light it has been approximately computed that the atmosphere does not extend beyond a height of 72·419 kilometres (45 miles) above the sea-level, and at that height the pressure would be 0.

The atmosphere appears of a blue colour, owing to the white sunlight being decomposed by particles of water contained in the atmosphere and reflected from them of a blue colour. The greater the quantity of light which is thus dispersed the brighter does the atmosphere appear, and it is brightest in the direction in which the greater number of particles are found, in which the atmospheric medium has the greatest extension and density—*i.e.* in a horizontal direction. On the contrary, the atmosphere is darkest in that direction in which the aërial stratum is thinnest—*i.e.* in a vertical direction. In fact the sky always appears much darker in the zenith than towards the horizon. Hence it happens that in ascending above the sea-level the sky becomes darker and at last entirely black. The stratum of atmospheric particles reflecting light becomes thinner and thinner, and in the same proportion does the lightless space beyond become more evident.

The red colour of the sky at sunset is caused by the aqueous vapour of the atmosphere. In a certain state of condensation it transmits white sunlight in shades between yellow and red. As the rays of the sun at evening have to traverse such vapour a longer distance, the sky appears of a hue varying from yellow to red.

One of the most interesting questions in respect to the atmosphere is whether the proportions by weight of the three gases, nitrogen, oxygen, and carbonic acid, always remain the same. Considering the immense quantities of carbonic acid poured into the air from the many sources of this gas, such as active volcanoes, processes of decay, combustion, animal respiration, etc., it might be thought that the amount of carbonic acid in the atmosphere would be constantly on the increase, while its contents of oxygen would be, on the other hand, decreasing. If that were the case, all animal life would ultimately perish from suffocation.

This production of carbonic acid and consumption of oxygen is, however, fully compensated by the action of plants, which, contrary to animals, absorb carbonic acid from the air, and exhale oxygen in its place. This action of plants is so energetic that, in plains where a tolerably luxuriant vegetation exists, the atmosphere always contains a somewhat smaller proportion of carbonic acid and more oxygen than the air of very high regions. On the whole, so far as can be deduced from analyses of air, the present composition of the atmosphere is kept in equilibrium by this vital action of plants.

When many persons remain for some time in a small and ill-ventilated room, analysis of the air contained in it certainly shows an increase of carbonic acid. However, in our dwelling-rooms, there is a greater change of air than is generally supposed, owing to the porosity of the walls. How readily air passes through an ordinary brick is evidenced by the following experiment: A brick is covered with wax, with the exception of the two opposite narrower extremities, and to each of these free ends is fastened an air-passage made of sheet-metal. By blowing through one of these passages the air can only escape by passing through the brick. This happens with such facility, that by blowing into the brick at one side it is easy to extinguish a lighted candle at the other side of the brick.

As in moist walls the pores are filled with water, rooms surrounded by such moist walls are unhealthy, because, amongst other reasons, the free passage of air is hindered.

Uses.—Atmospheric air is made use of in a great number of mechanical and chemical processes serving technical ends. From the most ancient times man has employed the motive power of wind—as, for instance, for turning the sails of windmills, for the purification of corn from dust and chaff, and in general for the separation of substances having different specific gravities by the agency of specially constructed vanes, by means of which the lighter bodies are got rid of.

Atmospheric air is further employed for drying purposes. The newly-built walls of houses, as well as a number of products of agriculture and manufactures, may be deprived of moisture by simple contact with the air. An important use is made of atmospheric air in getting rid of bad smelling and unhealthy gases and vapours from rooms occupied by human beings, often by means of artificial ventilation.

Atmospheric pressure is applied for forcing preservative or colouring solutions into the fibres of wood.

If the pressure of the air upon boiling liquids be diminished by conducting the operation of boiling in hermetically-closed vessels, from which the air is pumped out, evaporation takes place at a much lower temperature, and by this means solutions of a number of substances can be evaporated without undergoing decomposition, although many of them would be decomposed to a considerable extent if they were boiled or evaporated under the ordinary atmospheric pressure, and at the corresponding boiling temperature.

Atmospheric air plays an important part in the process of fermentation and its kindred phenomena of decay and putrefaction. It contains in the form of germs and spores the conditions for the production of ferments which bring about these processes, and in the form of oxygen gas a body which favours these processes in a high degree. It is often possible by admitting or excluding atmospheric air, either to start or prevent processes of the kind, and even to stop fermentation or putrefaction that has already begun, by subsequent exclusion of air. In various industrial operations advantage is frequently taken of these facts.

But the most extensive application of air is for the production of heat and light. Nearly all artificially produced heat and light are the results of processes of combustion, and in all these processes, the burning bodies, such as coal, fats, oil, coal-gas, etc., enter into combination with the oxygen of the air.

In the same way that rapid processes of oxidation with the evolution of light and heat take place in the air by the aid of the oxygen it contains, so likewise do gradual oxidising actions take place. The formation of nitrates may be instanced as one of the most important of these, the nitric acid being produced from ammonia by slow oxidation under the influence of air, in presence of bases, the ammonia itself being a product of the decay of nitrogenous organic substances.

The importance of air in the process of animal respiration has been already alluded to (p. 24).

CARBON.

Symbol C. Atomic Weight 12.

History.—Until the latter end of the eighteenth century, very little was known of the chemical nature or relations of carbon as an elementary substance, and it was not until Lavoisier demonstrated that carbonic acid gas—or fixed air as it was then called—is the sole gaseous product of the combustion, either of organic substances or of charcoal and the diamond, that correct opinions on this subject began to prevail.

Newton conjectured that the diamond must be combustible on account of its strong refraction of light. The first experiment by which the combustibility of the diamond was proved was made by the Academy of Florence, when it was found that a diamond burned in the focus of a large concave reflector. The diamond is not absolutely pure carbon, for after its combustion there remains a minute quantity of ash, which is said to contain silicic acid. The very small amount of this ash, and the high price of the diamond, have up to the present prevented a thorough determination of the ash, although that would be desirable, since an exact knowledge of the composition of this residue might afford some indications as to the substances out of which the diamond has been formed, and as to the manner of its formation, which is at present enveloped in uncertainty.

For some time it was supposed that besides carbon the diamond must contain hydrogen. This opinion was, however, refuted by the researches of Davy and others, which proved that by the combustion of the diamond in oxygen gas only carbonic acid, and no water, is produced.

Occurrence.—Carbon occurs naturally in the free state, but very much less abundantly than it occurs in various states of combination.

In the free state, carbon is met with in three very distinct conditions—as diamond and as graphite, which occur naturally, and as charcoal which is obtained in a great variety of forms when animal or vegetable materials are strongly heated out of contact with air.

Diamonds, or carbon crystals, are generally found in alluvial deposits of the most recent geological date, and situated at no great depth below the surface; they occur especially in the low ground of wide valleys, and but seldom in mountain districts of any great elevation.

Diamonds, as they occur in these alluvial beds, together with quartz pebbles, ferruginous sand, itaberite, brown iron ore, jasper, and sometimes also with topazes and emeralds, are never pure and sparkling, but always coated with an earthy incrustation, so that it is only with difficulty that they can be recognised by the naked eye.

The only diamond districts of importance, are East India, Brazil, and the Cape. There are also less extensive diamond yielding deposits in Siberia and the Island of Borneo. Recently, a diamond deposit has been found in Mundjee in New South Wales. The chief localities where diamonds occur in India, are situated in the kingdoms of Golconda and Visapur, extending down, however, towards Bengal. In Brazil, it is principally in the bed and on the shores of the river Igitonhona that diamonds are found in great quantity, especially in the district of Serro di Frio. Another diamond yielding stream in Brazil, is the Rio Pardo.

The Brazilian diamond washings yield annually from 25,000 to 30,000 carats, or nearly 13 pounds of raw diamonds, from which, however, only about 900 carats of finely polished diamonds are obtained.

Graphite occurs both in the amorphous and crystalline state. The amorphous variety called plumbago or blacklead, occurs at Borrowdale in Cumberland and at Passau in Bavaria; it is also found in Liberia, New Brunswick and other places. The crystalline variety occurs at Travancore in Ceylon, in Australia and in America.

Carbon also occurs naturally in the amorphous condition as anthracite, a mineral containing a much larger amount of carbon than ordinary coal, though closely related to it and most probably of similar origin.

In a state of combination carbon occurs very abundantly, constituting about one-third of the mass of all animals and plants. Carbon also occurs, combined with

varying proportions of hydrogen, oxygen, and nitrogen, in the form of coal and analogous materials, originating from plants belonging to a remote epoch. In combination with hydrogen, it occurs as petroleum and pit gas or marsh gas, substances intimately connected with coal and with the alteration of organised substances by decay.

In combination with oxygen carbon occurs in the atmosphere as carbonic acid, and though the proportion of this gas in atmospheric air is but small, this is the chief if not the only source from which plants derive carbon. This compound of carbon also occurs combined with various basic oxides, especially lime, magnesia, and ferrous oxide, as carbonates, in immense quantities, and it constitutes from one-ninth to one-seventh part of the vast masses of limestone and dolomite existing at different parts of the earth.

Characters.—Carbon in the free state is a solid infusible non-volatile substance without taste or odour; it exhibits very great diversity in some of the physical characters appertaining to it in the several conditions of diamond, graphite, and amorphous carbon or charcoal.

The diamond is distinguished from graphite, and still more from amorphous charcoal, by its crystalline structure, hardness, transparency, brilliancy, etc.

Carbon in the crystalline form of diamond is perfectly transparent, and possesses great brilliance. It is generally colourless, sometimes yellow or brown, and very rarely of a blue, green, or rose tint. The diamond is especially characterised by its hardness; for a long time it was held to be the hardest substance, and it is but recently that crystallised boron has been found to excel the diamond in hardness. The diamond has a specific gravity ranging from 3·50 to 3·55; it is infusible, and insoluble in all liquids.

The diamond occurs either in the form of crystals or as irregular rounded pebbles. The crystalline forms are the octahedron, the cube, the rhomboïdal dodecahedron, etc. The diamond pebbles generally have somewhat curved surfaces and blunt edges that appear to have been worn, and they are on that account very suitable for cutting glass.

The diamond refracts light either doubly or singly according to its outward crystalline structure. Besides its great refractive power, it possesses in a very high degree the property of dispersing coloured light after refraction and decomposition, and to this property is to be especially attributed the magnificent play of colours exhibited by the diamond.

If a diamond be heated to redness out of contact with air, or in a gas by which it is not chemically acted upon, it is not altered even by the highest temperature attainable, but still retains its characteristic properties. If, however, it be placed between the carbon terminals of a powerful galvanic battery, it is converted, with evolution of most brilliant light, into a graphite-like mass having a metallic lustre, which cannot be reconverted into diamond.

When heated in the air the diamond burns with great difficulty, the combustion beginning only at a temperature of about 1000° C. and then very sluggishly. It burns rapidly, however, in an atmosphere of oxygen. Indeed, when brought red-hot into this gas it burns without the application of further heat.

The largest known diamond is that of the Rajah of Mattan in the island of Borneo. It weighs 367 carats (carat = $3\frac{1}{6}$ grains troy), and is of the purest water. The diamond that was formerly in the possession of the Great Mogul, and supposed to be still in his country, weighed 279 carats, but it is said to have been reduced to about half its original weight by the process of polishing. Its value was estimated by Tavernier to be about 420,000*l.* The Emperor of Russia has in his possession a diamond which weighs 193 carats. It was bought in 1772 by the Empress Catherine of a Greek merchant for the sum of 90,000*l.* besides an annuity to the Greek merchant of 4,000*l.* The diamond in the possession of the Emperor of Austria weighs 139 carats; the Regent or Pitt diamond of the late Emperor of the French weighs 136 carats. The former is valued at about 105,000*l.*, the latter at about 97,500*l.*, or according to other estimates at 185,000*l.*

The diamond called the Koh-i-noor (mountain of light) weighs 186 carats. The opinion that the Koh-i-noor is identical with the Great Mogul appears to be incorrect, since the sketch which Tavernier gave of the Great Mogul represents this diamond as differing considerably in form from the Koh-i-noor.

Graphite sometimes possesses a definite crystalline form, but it belongs to a system entirely different from that of the diamond. Graphite is opaque, of a black or grey colour; it has a metallic lustre and is a good conductor of heat and electricity, while the diamond is not so good a conductor of heat as graphite, and is a non-conductor of electricity. The specific gravity of graphite varies from 1·8 to 2·4.

Amorphous carbon in the form of anthracite, is a hard black substance possessing considerable lustre. It has a laminated structure, gives a black streak on paper, and is very friable. Its specific gravity is from 1·3 to 1·8.

When substances containing carbon in combination with hydrogen and oxygen

sometimes also with nitrogen, sulphur, etc., are strongly heated out of contact with air, hydrogen, oxygen, nitrogen, and sulphur escape, together with a portion of the carbon in the form of various volatile compounds, but the greater part of the carbon remains behind as charcoal. This charcoal contains, besides the ash-constituents of the organic substance, also a small quantity of hydrogen, which clings to the residual carbon so strongly, that it must be kept at a white heat for a considerable time before it gives up the last portion of hydrogen. If it be desired to prepare chemically pure carbon, pure organic compounds must be employed. Thus for instance, sugar after being heated in a closed vessel for a long time, and the residue eventually exposed to a white heat, yields chemically pure carbon. Amorphous charcoal, obtained by the heating of organic substances with exclusion of air, is a good conductor of electricity and a bad conductor of heat.

When a carburetted gas, or the vapour of a volatilisable organic substance, is passed through a red hot tube it is decomposed, and carbon is deposited upon the inner surface of the tube. If such a deposition of carbon continues gradually for a considerable length of time, the deposited carbon forms a very dense, compact hard crust. Carbon in this condition, is found in the retorts used in the manufacture of coal-gas, and it is sometimes sufficiently hard to scratch glass.

The carbon obtained from any organic substance by heating it out of contact with air, is always amorphous and generally soft and friable. It is further black and opaque, and the fracture is sometimes lustrous, but more generally dull. Its specific gravity varies from 1·5 to 2·0; the compact carbon deposited in gas retorts has sometimes a density of 2·36.

Some kinds of charcoal present no indication of the form and structure of the organic substances they are obtained from, and the carbonaceous residue is either spongy, vesicular, or porous, as that from gum, sugar, starch, and other substances. In this case, the charcoal presents that form which the carbonised substances assumed at the moment of carbonisation. If these substances first of all melt upon the application of heat, the molten mass froths in consequence of the escape of gases, and as this aerated mass solidifies in carbonisation, it retains its spongy texture.

Charcoal in a pulverulent form is obtained when infusible substances in a finely-divided state are carbonised, as, for instance, saw-dust; further, when an organic substance is mixed with a large quantity of a refractory body in a state of fine division, such as sand. Carbon is obtained in the finest state of division when it is deposited from a gas in a state of imperfect combustion, as, for instance, when the flame of highly carbonaceous materials, such as pitch, tar, etc., burnt with a limited supply of air, is suddenly cooled. Soot, lamp-black, etc., consist of carbon in this condition.

The characters which the three modifications of carbon possess in common are the following: they are solid, without taste or smell; when heated out of contact with air they are unaltered, and they resist the action of every known solvent, but when heated in contact with air they burn, yielding carbonic acid.

As regards combustibility the three modifications of carbon present considerable differences; for while charcoal burns easily when heated in the air, graphite, and more especially diamond, can only be burnt when exposed to the highest temperatures.

Carbon does not manifest any marked chemical activity at ordinary temperatures. A very remarkable proof, amongst others, of this, is to be found in the unaltered state of the ink upon manuscripts found in Herculaneum, which are about 2,000 years old. This ink consists of finally divided carbon that had been ground up with some mucilaginous liquid. This unchangeability of carbon is the reason why wood that has been superficially carbonised, lasts even in moist earth for a very long time without decaying.

At high temperatures, however, carbon combines readily with oxygen and forms carbon dioxide, a gaseous compound equal in volume to the oxygen combined with the carbon; but carbon does not burn with flame because it is incapable of volatilising.

According to the conditions under which carbon is burnt, two different products may be produced. If it be burnt with an abundant supply of air, or as is commonly the case in contact with a large excess of air, it combines with 2·67 times its weight of oxygen, forming carbonic acid, CO_2. On the contrary when carbon is burnt with a deficient supply of air, the lower product of oxidation, carbonic oxide, CO, is formed either entirely or to a great extent; in the application of carbon for heating purposes it is therefore one of the chief conditions that so much oxygen shall be supplied to the burning carbon, that it may be entirely converted into carbonic acid.

Besides the direct combination with free oxygen, which takes place when carbon or any combustible carbonaceous substance is burnt in atmospheric air, carbon is, under certain conditions, also capable of abstracting oxygen from many compounds, and combining with it. Thus, for instance, at a bright red heat carbon decomposes carbonic dioxide, combining with half of its oxygen, and thus converting it into carbonic oxide,

$CO_2 + C = 2CO$, while at the same time forming an additional quantity of the same substance. Water-vapour is also decomposed by carbon at a red heat, the oxygen combining with carbon, while the hydrogen is separated in the free state. Carbon combines in like manner with part or the whole of the oxygen of most metallic oxides, when heated in contact with them to a sufficiently high temperature, and in many cases the metals are reduced or separated in the free state as regulus. This process is termed reduction, and the capability of effecting deoxidation in this way is a character that renders carbon a very useful agent in many industrial operations.

Other compound substances containing oxygen, such as sulphuric, nitric, and other oxyacids, as well as their corresponding salts, are decomposed in the same manner when heated with carbon. The deoxidation thus effected is often only partial, as in the case of sulphuric acid, which yields, when heated with carbon, a mixture of sulphurous acid and carbonic dioxide. The metallic salts may, however, be completely deoxidised by heating them with excess of carbon, and then the metals often remain combined with the other elementary constituents of the acid oxides, if the compound is not itself decomposed by the high temperature required. In such cases the carbonic dioxide formed in the first instance is decomposed by contact with the excess of carbon, and converted into carbonic oxide. Thus barium sulphate yields barium sulphide and carbonic oxide, when ignited with carbon. $BaSO_4 + 4C = BaS + 4CO$. When nitrates, chlorates, iodates, etc., are heated with carbon or carbonaceous substances, the combination of their oxygen with carbon takes place suddenly and with explosive violence and great evolution of heat, rendering the mass red hot. This phenomenon is called deflagration.

Carbon also combines directly with sulphur vapour at a red heat, forming carbon disulphide, CS_2.

In the presence of alkaline substances, and at high temperatures, carbon combines with nitrogen, forming cyanogen, CN. Under the influence of the electric arc, it combines with hydrogen, forming acetylene, C_2H_2, and at very high temperature, it combines in small proportion with some metals, for instance, in the manufacture of iron, which always contains a small amount of carbon.

Coke.—This form of carbon, is obtained by heating certain kinds of coal out of access of air. The process is entirely analogous to that of the carbonisation of wood; hydrogen and oxygen, contained in the coal, are driven off chiefly in the form of water, together with a certain amount of carbon in the form of hydrocarbons and other volatile carbon compounds, while the greater portion of the carbon remains mixed with the mineral constituents of the coal. As compared with coal, coke is generally very hard (sometimes even scratching glass), compact, and lustrous; its colour varies between grey and black; it is also a good conductor of electricity and heat. In consequence of the very compact texture of coke, it is difficult to set fire to it, and consequently, when used as fuel, it requires a good draught or a blast for maintaining its combustion. When once in a state of combustion, it produces a very considerable degree of heat.

According to the kind of coal carbonised, as well as the mode of conducting the operation, coke presents very diverse characters, being more or less compact or vesicular, hard or friable, and sometimes even pulverulent.

Wood Charcoal.—Charcoal often retains the form and structure of the organic substance from which it is prepared. This is especially the case with wood charcoal, which always shows quite distinctly the structure of the wood that has been carbonised.

But though wood charcoal presents, in ite outward appearance, the peculiarities of the wood from which it has been made, the charcoal of a particular kind of wood is not always of the same character, but varies somewhat according to the age of the wood, and the conditions under which it has been grown, partly also according to the temperature at which the carbonisation has been conducted. The denser the wood, and the drier the soil upon which it has been grown, the denser is the charcoal it yields. Charcoal is also denser the higher the temperature of carbonisation.

A knowledge of these facts is of practical importance. If it be desired, for instance, to produce charcoal which shall conduct electricity, only such charcoal is serviceable for the purpose as has been prepared at the highest possible temperature, for it is only the denser kind of charcoal that is a good conductor of electricity. On the other hand, when readily combustible charcoal is required, the carbonisation must not be carried on at too high a temperature, since the denser sorts of charcoal burn with difficulty.

Charcoal, like all porous substances, possesses the property of absorbing gases into its pores. The more porous the charcoal, the greater is its absorbent power, and on that account, wood charcoal possesses this property in the highest degree. The absorption of gases by charcoal at a temperature of 100° is very slight, but it

begins at a temperature very little below 100°, and increases as the temperature falls. It follows therefore that, by the application of heat, the whole absorbed gas may be expelled from charcoal that has become saturated with any gas at the ordinary temperature. In like manner, the gas absorbed by charcoal escapes when the charcoal is placed in vacuum.

In order to determine the absorbent action of charcoal in reference to any particular gas, a piece of charcoal that has been freshly heated to redness is weighed, and then placed in a graduated glass cylinder containing the gas and inverted over mercury. Owing to the absorption of the gas, part of it disappears, and the diminution of volume indicates the absorbing power of charcoal for the particular gas.

Although wood charcoal possesses the greatest absorbent power of all varieties of charcoal, still this capacity of absorption varies considerably, according to the kind of wood from which the charcoal has been prepared. Very light kinds of charcoal, with very large pores, as well as very dense kinds, absorb very much less of a gas than charcoal of average porosity. For instance, the light charcoal of pine wood, with very large pores, absorbs only half as much gas as the more dense charcoal prepared from oak wood. The mechanical division of the charcoal is in like manner of importance. Very finely powdered charcoal, as well as very large pieces of charcoal, condense less gas than moderate sized pieces. The reason of this is obvious. In very fine charcoal powder, the pores are lessened by a too great state of division; in large pieces, the communication of the pores from their interior to the surface, is rendered very difficult, on account of the distance; some of the pores do not communicate with the surface at all, while in the smaller pieces, more of the pores are exposed, and communicate with the surface. The charcoal of cocoanut shell appears to have the greatest capacity of absorbing gases.

When charcoal is already saturated with a gas, it absorbs extremely little of any other kind; on this account, charcoal exposed to the air loses its absorbent property, by becoming saturated with gases contained in the atmosphere, and it is only fit for use as an absorbing agent soon after having been heated to redness. The amount of different gases that the same kind of charcoal, when freshly heated to redness, is capable of absorbing varies considerably, as shown by the following table.

Beechwood Charcoal (Saussure).			Cocoanut Charcoal (Hunter).
90	times its volume	of ammonia gas	171·7
85	„	of hydrochloric oxide gas	
65	„	of sulphurous oxide	
55	„	of sulphuretted hydrogen	
40	„	of nitrous oxide	
35	„	of carbonic dioxide	67·7
9·4	„	of carbonic oxide	21·2
9·25	„	of oxygen	17·9
7·5	„	of nitrogen	
1·75	„	of hydrogen.	

Freshly burnt charcoal, or charcoal freshly heated to redness, can therefore be used for removing from rooms injurious and bad smelling gases.

In consequence of the condensation of gases in the pores of charcoal, the chemical activity of these gases is often augmented in a high degree. Thus, for instance, if a piece of wood charcoal saturated with suphuretted hydrogen gas be placed in an atmosphere of oxygen, a violent reaction takes place, sometimes amounting to explosion, water and sulphurous acid being produced. If ordinary atmospheric air be employed in the place of pure oxygen, the oxygen it contains combines more slowly with the hydrogen of suphuretted hydrogen, but not with the sulphur, which is therefore deposited. This reaction occurs frequently where air comes into contact with sulphuretted hydrogen in the presence of porous substances.

The oxygen of atmospheric air absorbed by charcoal is converted into carbonic dioxide by combining with the carbon, and consequently the gas expelled from charcoal that has been exposed to the air for some time consists entirely of nitrogen and carbon dioxide.

Since charcoal absorbs most fetid substances with great energy, the absorbent action of charcoal is also taken advantage of in order to remove bad smelling impurities from liquids, in the same way that it is made useful in removing bad odours from the air. In order, for example, to deprive crude alcohol made from corn, or potatoes, of the unpleasant fusel oil it is contaminated with, the spirit is allowed to remain a short time in contact with charcoal, before being distilled (*vide* 'Alcohol').

Charcoal lying exposed to the air, absorbs moisture; and this takes place with such rapidity, that in course of only a few days, the charcoal will have taken up from the air as much water as it is capable of absorbing.

According to Chevreuse, 100 parts of charcoal exposed to an atmosphere almost saturated with moisture, exhibit the following degrees of absorption:

	Charcoal of poplar wood: not heated to redness.	Charcoal of poplar wood: heated to redness.	Charcoal of guaiacum wood: not heated to redness.	Charcoal of guaiacum wood: heated to redness.
1st day . .	1·76	1·53	0·58	0·21
3rd day . .	2·35	2·30	0·82	0·40
30th day. .	2·35	2·35	1·19	0·94

When charcoal is immersed in water, it absorbs much more. In this case, the absorption is, for 100 parts:

Of poplar wood charcoal, not heated to redness	75·3
Of „ heated to redness . . .	48·2
Of guaiacum wood charcoal, not heated to redness . . .	7·7
Of „ heated to redness . . .	4·6

Since charcoal is sold by weight, regard must be had to its property for absorbing water: for any water thus absorbed, has a double disadvantage, inasmuch as it not only increases the weight of the charcoal, but having also to be evaporated, it lessens its heating effect. The charcoal of commerce is never entirely free from mechanically adhering water, but always contains from eight to twelve per cent of water.

Animal Charcoal.—A further peculiar action of charcoal is exercised upon dissolved colouring matters, especially by bone charcoal, which deprives most coloured liquids of their colour-substances, by condensing them into its pores. Thus, red wine, solutions of cochineal or madder, or a neutral solution of indigo in sulphuric acid, etc., may be decolorised by charcoal. This decolorising action of charcoal is frequently employed on a large scale in various industrial operations, especially in the manufacture of sugar, for decolorising the cane-juice in the preparation of raw sugar and for decolorising the solution of raw sugar in refining (*vide* 'Sugar Manufacture').

The various kinds of charcoal differ very considerably in regard to their respective decolorising powers. The charcoal most efficacious for decolorising is the nitrogenous charcoal obtained by carbonising bones or other animal substances, and it is this kind chiefly that is practically employed for the purpose.

The decolorising action of charcoal was discovered in the year 1790 by the Russian chemist Lowitz. By the year 1798, this property of charcoal was already turned to account in the sugar manufacture, it being employed in the decolorisation of the beet juice. Wood charcoal, however, which at that time was exclusively used, accomplished this end only imperfectly; but in 1811, Figuier of Montpellier discovered that animal charcoal had a much more powerful decolorising action than wood charcoal, and two years later its use was introduced by Derosne, Payen, and Pluvinet, into the sugar manufacture in the place of that of wood charcoal.

When charcoal is saturated with colouring matter, it does not exercise any further decolorising action; but, if the colour-substances it has absorbed be separated by solvents or destroyed, either by fermentation or by heating the charcoal to redness with exclusion of air, it again acquires its decolorising power. This process is termed the **revivification** of the charcoal.

Preparation.—A number of different methods of preparing carbon are practised for various purposes, but all of them consist essentially of subjecting combustible carbonaceous materials to the action of heat, either entirely out of contact with atmospheric air, or in such a way that the supply of air is only sufficient for the combustion of the volatilisable portion of the materials. In a general way, this process is termed **carbonisation** or **charring**. It is practised most extensively for the purpose of rendering certain materials more suitable for use as fuel in many metallurgical, and other operations.

Wood Charcoal.—The carbonisation or charring of wood, is generally carried out in heaps, or piles built up of logs or billets of wood, arranged either vertically or horizontally, and covered with earth in order to keep out air. The heat required is produced by setting fire to the heap at the interior, and allowing a portion of the wood to burn slowly with a very limited supply of air, in such a way that the requisite heat is produced by the wood which is undergoing carbonisation. In this carbonising process, volatile by-products are produced (pyroligneous acid, tar, etc.), and as these are of value, the carbonisation of wood is, in many cases, carried out in closed ovens, provided with condensing apparatus for the condensation of the volatile products.

The mode of heating wood has very great influence upon the amount of charcoal produced. If wood be heated in such a way that the temperature rises gradually, more charcoal is obtained than when the wood is rapidly brought to a high temperature. Karsten obtained the following results from comparative experiments made in this direction.

Kind of Wood Charred.	Percentage amount of Charcoal obtained.	
	Rapid heating.	Slow heating.
Young oak wood	16·54	25·60
Old oak wood	15·91	25·71
Young red beech wood	14·87	25·87
Old red beech wood	14·15	26·15
Young white beech wood	13·12	25·22
Old white beech wood	13·65	26·45
Young alder wood	14·45	25·65
Old alder wood	15·30	25·65
Young birch wood	13·05	25·05
Old birch wood	12·20	24·70
Young pine wood	14·25	25·25
Old pine wood	14·05	25·00
Young fir wood	16·22	27·72
Old fir wood	15·35	24·75
Young Scotch fir wood	15·52	26·07
Old Scotch fir wood	13·75	25·95
Lime wood	13·30	24·60

Coke.—The carbonisation of coal is conducted very much in the same manner as wood charcoal is prepared, and with the same general result of obtaining a material consisting chiefly of carbon. But in addition to the separation of the volatilisable portion of coal by which that result is produced, the carbonisation of coal has, in many cases, a further important influence upon its applicability as fuel for many purposes. This consists in the total or partial separation of the sulphur, with which some kinds of coal are largely contaminated in the state of pyrites, a mineral consisting of sulphur in combination with iron. At the temperature requisite for carbonising coal, this substance is decomposed, giving off a considerable portion of its sulphur, which escapes with the other volatilised products of carbonisation.

Coke is prepared both in heaps or ridges like wood charcoal and in close ovens; but when coke is prepared for use as fuel, the ovens are never heated externally for the purpose of effecting the carbonisation, as is sometimes the case with wood.

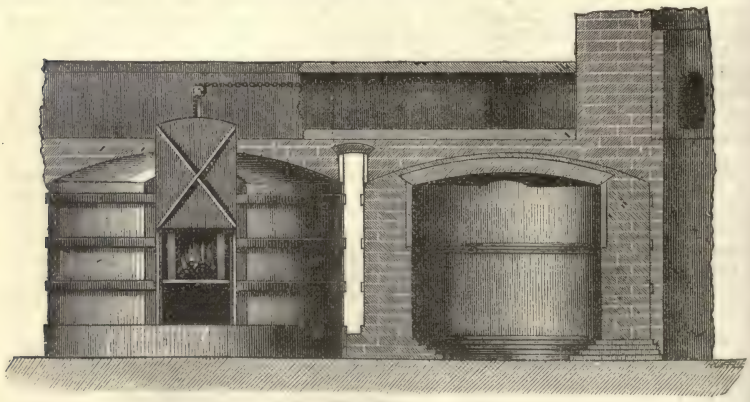


Fig. 21.

The coke ovens employed for carbonising coal, are generally large arched chambers of strong brickwork, with a door in front for charging in the coal and an aperture on the crown of the arch for the escape of the volatilised products of carbonisation. A range of such ovens is represented by fig. 21.

In using these ovens for making coke, they are first made red hot by burning fuel in them, and then are charged with a sufficient quantity of raw coal, which is ignited by the hot brickwork, and is allowed to burn by keeping the front doors of the ovens open as long as dense smoke or flame escapes through the aperture at the top of the ovens. When this discharge of smoke and flame has nearly subsided, the doors are closed and the apertures at the top covered up. The ovens are left in this condition for several hours, and then water is thrown upon the incandescent mass of coke, to cool it sufficiently for its being drawn out without continuing to burn.

Animal Charcoal.—The manufacture of animal charcoal is generally carried on in the neighbourhood of large towns, because it is in such places that the requisite supply of bones can be best secured.

When bones are heated, the organic substances are decomposed and carbonised. Volatile substances are formed, some of which are combustible gases that do not condense upon cooling, but escape, while others condense and form a heavy oily layer (bone oil) and an aqueous layer, which has a tarry smell and colour, and contains ammoniacal salts in solution. In the residue are found the inorganic constituents of the bones, uniformly mixed with more or less finely divided carbon, and constituting animal charcoal. Upon heating this in the air the carbon is burned and the inorganic constituents of the bones remain as a grey or white substance, known as bone ash. But if the charcoal be treated with warm dilute hydrochloric acid, the inorganic salts are removed and pure carbon remains behind.

The carbonised bone, coarsely powdered, is used under the name of animal black for decolorising purposes; finely powdered, it is termed burnt ivory or bone black, and is used in the production of black paint, and especially of blacking for boots.

The carbonisation is conducted differently according as it is desired to obtain only the charcoal, or to collect also the condensible volatile products. In the latter case the carbonisation is conducted in retorts like those used in the production of wood vinegar (*vide* 'Acetic Acid'), and the watery distillate can be worked for ammonium salts (chloride and sulphate). If the operation is confined to obtaining the non-volatile animal charcoal, only a simple apparatus is necessary, and an important saving in fuel is effected.

According to the method at one time generally adopted, cast-iron crucibles 12 inches in diameter and 16 inches high were used. These crucibles, filled with broken-up bones, were put into large furnaces, five crucibles being placed one on another, so that the covers of the lower ones were formed by the crucible next above them, and only the top crucible required a special lid. More recently, crucibles made of fire-clay have been used, the size and form remaining the same. These fire-clay crucibles have the advantage, that from an equal quantity of bones more charcoal is obtained, because they do not lose their round form upon being heated. Consequently they fit closer upon one another, less air can penetrate, and therefore less charcoal is burnt. Moreover, since the clay is a bad condenser of heat, the carbonisation takes place more slowly in the fire-clay crucibles, and less volatile products are formed.

It has also been found advantageous not to place the crucibles one upon another, but side by side; only one row of crucibles being then placed in the furnace. With the exception of the height of the oven, the other arrangements remain the same.

The furnace consists of a flat hearth, having a superficial area of about 40 square yards, covered in with a flat arch. The fireplace is in the middle of this space; the crucibles are introduced and removed through doors at the front upon ironbars, let in to the brickwork, and they are easily moved to and fro by means of long hooked rods. Each furnace holds eighteen crucibles. The lids are luted on to the crucibles with clay. As soon as the furnace is filled, the doors are bricked up with a double row of bricks.

It is advisable to build several such furnaces adjoining each other, and especially to couple two back to back, so as to economise heat and fuel. It is advantageous also to have a revivification furnace between two pair of carbonising furnaces, so that the flame of the four furnaces serves for the heating of the fifth.

When the crucibles have been placed in the furnace, the temperature is gradually raised to a red heat, and is maintained at that point for six or eight hours. As soon as the decomposition of the bones commences, a large quantity of combustible vapour is evolved, which takes fire and burns in the furnace. So much heat is thus developed that only a small quantity of fuel is required. When the decomposition is completed the crucibles are drawn without waiting for the cooling of the oven, and the furnace is at once charged with fresh crucibles, whilst the others are cooling.

A uniform and sufficient temperature is especially important in the carbonisation of bones. Insufficient heating yields a charcoal containing a portion of organic sub-

stance not yet decomposed, which dissolves in the aqueous fluid to be decolorised and communicates to it a strong loathsome smell. A charcoal burnt at too high or too long continued a temperature yields too dense a product, the surface exposed, and therefore the decolorising power of the charcoal, being proportionally reduced. It is consequently necessary not only to burn the bones sufficiently, but also to prevent the temperature from rising too high.

In two furnaces such as are here described, more than a ton of bones can be carbonised at one time, and four charges may be worked daily. The yield is about 60 per cent., or altogether about 2½ tons of animal charcoal.

After cooling in the crucible, the charcoal is crushed. If it be required for decolorising purposes, care must be taken to avoid as much as possible the production of a fine powder, as this is less valuable than charcoal in small lumps. In order to obtain the charcoal in lumps rather than in powder, the burnt bones are broken up by means of grooved rollers consisting of toothed disks alternately of 10 and 12 inches in diameter. Two such cylinders are so arranged that the smaller disks of one are opposite the larger disks of the other, and in revolving, the bones are crushed between them without being pulverised. To obtain the charcoal in sufficiently small lumps without much fine powder, the bones are passed through six of these mills, the rollers of each successive mill being set closer together than those of the previous one. By an arrangement of sieves, the fine powder is separated from the lumps, and these are again separated according to their size.

Bones are sometimes carbonised in perpendicular iron cylinders, several of which are heated by one common fire. At the bottom of each cylinder is a slide for the removal of the charcoal; on the top is a lid with a tube for evolved gases and vapour. These tubes extend into the flue by which the distillation products escape. The charging of the cylinders is effected from above through the lids, which are then luted with clay. After heating for two hours, the charcoal is withdrawn by opening the slides underneath; it is cooled in iron boxes closed from the air as much as possible. These retorts can be so arranged that the distillation products are condensed and thereby gained in addition.

The preparation of animal charcoal can also be carried on in combination with that of gas for lighting. This method, however, has not hitherto presented sufficient advantages over the manufacture of such gas from other materials.

Lamp-black.—The finely divided carbon known as lamp-black is prepared on a large scale in the following manner. Fat, oil, rosin or resinous wood, tar, etc., are allowed to burn with an imperfect supply of air, either in a brick furnace, or in cast-iron chambers, and the products of combustion are conducted through a long brickwork flue into a large chamber of timber or brickwork. From the ceiling of this chamber is suspended a large hood of woollen cloth, which nearly fills the chamber, and upon its surface most of the lamp-black is deposited; only the loose light soot finds its way into this chamber, the more dense or heavy soot remaining behind in the brickwork flue. In many places, the products of combustion, after being evolved in the flue, are conducted through a number of sacks placed in connection with it, in which the lamp-black is collected.

In some districts of France, lamp-black is obtained in a very simple way. Resinous substances are burnt in a wooden chamber, the walls of which are hung with coarse cloth. The resinous materials are ignited in vessels of clay or iron. The soot produced deposits itself upon the rough surface of the cloth, from which it is afterwards scraped off.

An especially fine quality of lamp-black is obtained from oil, waste fat, mineral oils, and the like, by means of lamps constructed for the purpose.

The arrangement of an apparatus of this kind is shown by figs. 22 and 23. The vessel (A) contains oil, the level of which is kept constant by means of a globular vessel (B) also filled with oil, and inverted over A. From the vessel (A) the oil flows into the tube (C), bent at right angles at its other extremity, which must be on a level with the oil in A. This tube is furnished with a cotton wick, and at c' is a spout, by means of which any overflowing oil is conducted into the vessel c'' placed beneath it. The flame is surrounded by a conical hood (d), which terminates in a tube (d'). Through this tube, the sooty products of combustion are conducted into the broad horizontal tube ($d''d''$). This latter tube receives the products of combustion from eight or ten or more lamps placed at intervals of about six feet from one another, as shown by fig. 23.

The wide tube (d') serves to cool the smoke, as well as to collect water and other liquids) which the smoke deposits. From this tube, the smoke passes into the first sack (e) made of linen of close texture, the length of which is about ten to twelve feet, and the diameter three feet: this is closed below with a trap or slide (e'). The upper

and lower ends of the sack consist of funnel-shaped tubes, made of sheet copper. The upper tube terminates in a further additional pipe (*f*), through which the smoke passes into the second sack (*g*), which has exactly the same construction as the first. From the second sack, the smoke finds its way into the third; from thence through *k*, and so on, into the last (*o*).

The lower extremity of the last sack of each row is connected with a horizontal flue (P), containing frames covered with wire gauze, and mounted on hinges. This

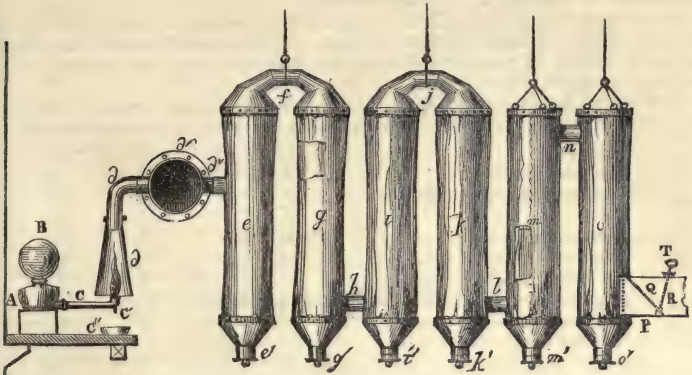


FIG. 22.

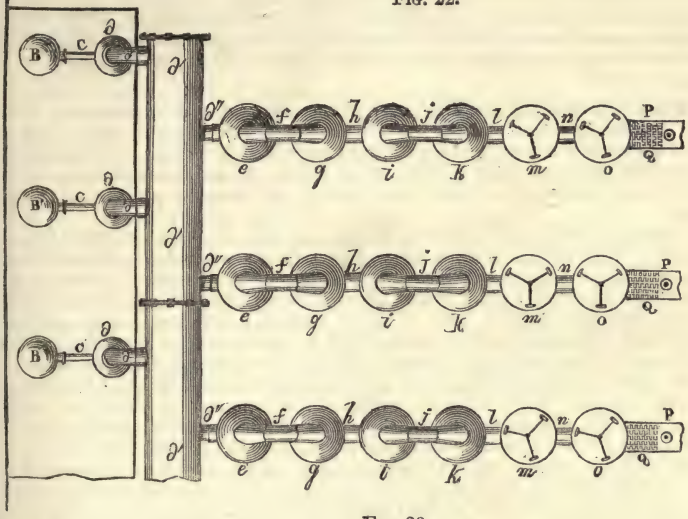


FIG. 23.

arrangement serves to retain the last portions of lamp-black carried over with the smoke from the sack. Since the wire gauze (Q) very soon becomes choked with soot, the draught is checked and it has to be cleaned at intervals: this operation is performed by means of the rod (T), which being raised and allowed to fall suddenly, jerks the soot off the sieve. The other end of the flue (P) terminates in a chimney, by which the draught of air flowing through the entire apparatus can be regulated.

The removal of the black is effected by opening the mouth-pieces at the lower end of the sacks, and shaking out the contents.

This arrangement admits of the products of the different sacks being separately collected. The product in the first sack is generally kept apart from that of the rest, as it is not so pure, containing resinous or tarry substances.

In the neighbourhood of Saarbrücken, a coarse sort of lamp-black is obtained by the combustion of highly bituminous coal. The apparatus consists of a long slightly

ascending brickwork flue, in which the coal is burnt with a supply of air insufficient for complete combustion. The sooty products of combustion pass into a vaulted chamber, where a part of the soot is deposited. This chamber is connected with three others, decreasing in size, and placed vertically above one another. The products obtained from each of the three chambers are collected separately, since they differ in quality, the best being found in the last chamber. The amount of lamp-black thus obtained is very small: one thousand parts of coal yielding only about thirty-three parts of lamp-black. The coke obtained at the same time, and amounting to about 40 or 50 per cent., is, however, a valuable product.

Before lamp-black is packed, it has generally to undergo the operation of sifting. It is packed either in sacks, barrels, or casks. If it be packed in sacks, they should be previously soaked in water containing clay, which stops up the meshes, and thus prevents loss of the lamp-black.

Commercial lamp-black is not altogether pure carbon: but always contains small proportions of other substances, as shown by the following analysis by Braconnot:

Carbon	79·1
Resinous substances	5·3
Combustible oily substances	1·7
Ulmin	0·5
Ammonium sulphate	3·3
Potassium sulphate	0·4
Calcium sulphate	0·8
Calcium phosphate (containing a large percentage of iron)	0·3
Potassium chloride	traces
Silicious sand	0·6
Water	8·0

Commercial lamp-black can be purified by heating it to redness in well-closed crucibles or cylinders, to decompose resin and other organic substances. In order to get rid of mineral substances, it must be treated with hydrochloric acid, and the excess of acid afterwards removed by frequent washing with water. After lamp-black has gone through these processes, pure carbon remains, contaminated only with a very small quantity of sand.

Uses.—Besides the extreme rarity of the diamond and its hardness, which is only excelled by boron, its lustre and refractive power also add to its high value. Until the method of cutting and polishing rough diamonds was known, they possessed a comparatively small value. It is curious that the Roman stone polishers made use of diamond powder for polishing other stones, but never for polishing the diamond itself.

The art of cutting and polishing the diamond was discovered in 1476 by Louis de Berguen. This substance can be easily split in the direction of the octahedral surfaces of a regular octahedron, and since the grinding of diamonds is an extremely tedious operation, advantage is taken of this cleavage in order to give them before polishing the approximately desired form. For this purpose it is necessary to determine the direction of the cleavage of the diamond with precision, and this requires great experience as well as great manipulative skill. When the direction of cleavage is ascertained, the parts to be removed are split off by the application of a knife aided by a blow with a small hammer. This being accomplished, the formation of facets is proceeded with. For this purpose, the diamond is so fastened in the end of a stick, or handle, of iron by means of a cement made of tin solder that the part which is to be ground down is left projecting. This projecting part is rubbed with strong pressure against a second diamond also fixed in a similar manner, and thus the two stones are mutually abraded and acquire the flat surfaces or facettes desired. Other facettes are formed in like manner after shifting the diamond into fresh positions in the cement.

The last operation of polishing is executed in the following way. The diamond to be polished, is fastened in a small socket of copper with tin solder, and by means of a special contrivance this socket is pressed against a rapidly rotating disc of steel, upon the surface of which a small quantity of diamond powder (bort) mixed with oil, has been previously placed. The polishing is continued until a facette is complete, then the stone is reset and the other facets polished in like manner.

The bort is obtained, either by the mutual abrasion of rough diamonds or by crushing useless diamonds and diamond chippings to powder in a steel mortar.

Some diamonds are so hard that they cannot be polished. These can only be used as glazier's diamonds, or for polishing other diamonds and precious stones.

The most simple form of the polished diamond is that of the rose, which is flat beneath, while the upper portion, which has in all 24 facets, forms a pyramid having triangular faces.

A more valued form of the diamond is the brilliant, the greatest diameter of which is at two-thirds of its height. The upper part which projects beyond the setting and is termed the pavilion or crown is half the height of the under part within the setting which is termed the collet (culasse).

Besides the application of diamonds for purposes of dress and decoration, as being the most valuable of all precious stones, they are of considerable use industrially. On account of their great hardness they are used as bearings for the pivots of delicate watches. They serve further, as has already been mentioned, for polishing other precious stones, for drilling, rock boring, and especially for cutting glass.

For a long time it was supposed that the action of the diamond in cutting glass depended upon the hardness of the diamond and upon its simply scratching when it was passed over the surface of a piece of glass; but Wollaston's researches showed that in cutting glass with a diamond, though the rounded edge of the diamond certainly does in the first instance scratch the glass, it then penetrates the glass like a wedge and thus produces, under the part scratched, a continuous crack. It is for this reason that polished diamonds with perfectly even faces are useless for the purposes of the glazier, it being necessary, in order that the diamond may act like a wedge, that the edge made use of should be formed by curved faces, as is the case in the rough diamond.

One of the chief applications of graphite is for making lead pencils. Graphite is also used, mixed with clay, for the production of plumbago crucibles, which are capable of bearing a high temperature.

Carbon has long been employed in drawing and writing. The most suitable kind for this purpose is vegetable charcoal; for owing to its softness, it more readily makes a mark upon paper. In ancient times, ink was prepared from wood charcoal, which was first finely powdered, and then mixed with a mucilaginous liquid.

China ink, or Indian ink, as it is called, is prepared from the soot obtained by burning the oil of *Sesamum orientale*, less frequently from other forms of soot, mixed with size or gum water, and dried. Frequently, the ink is mixed with some aromatic material, such as camphor; but its essential characters are not thereby altered. Printers' ink consists of carbon in a very fine state of division, mixed with boiled linseed oil to a thin pap.

The other pigments made of vegetable charcoal are named according to their origin, since they present different degrees of density and blackness, according to the material from which they are prepared.

For instance, vine black is obtained by carbonising the wood of the grape vine. Spanish black consists of the carbon of cork chippings. It is a charcoal, remarkable for its great softness and loose consistency.

Charcoal crayons are made of alder-wood charcoal, obtained by carbonising suitable pieces of the wood of the alder in iron cylinders heated to redness, and closed so as to leave only a small aperture for the escape of the products of distillation.

Frankfort black is the carbon obtained from a mixture of vine twigs, lees of wine, and sometimes also peach stones, bones, and ivory refuse. According as the vegetable or animal charcoal is predominant, so do the pigments vary in shade: when vegetable charcoal is predominant, it has a bluish hue, and a brownish tinge when there is a preponderance of animal charcoal. As a rule, soluble mineral substances are generally removed by washing before the charcoal is used. This black is used in copper-plate printing.

Lamp-black, or the finely divided carbon obtained by imperfect combustion of fats, oils, resins, pitch, coal, etc., is chiefly used as a pigment.

The consumption of animal black every year acquires greater dimensions. It is used in sugar manufactories, for the decolorisation of the juice and of the syrup in the working of the after products, as well as in the refining. The use of animal black in sugar boiling has also been commenced in the colonies.

An important application is made of carbon in metallurgy, on account of its capability of abstracting oxygen from metallic oxides, and in fact it is either directly or indirectly the principal reducing agent employed for this purpose in metallurgical operations.

But the chief application of carbon, or of combustible carbonaceous materials, is for use as fuel to produce heat.

Compounds.—Carbon forms a number of compounds with other elementary substances, and some of the more complex compounds of carbon, such as vegetable acids, alcohols, starch, sugar, cellulose, albumin, casein, etc., constitute a peculiar class of substances, which are termed organic substances, since they are generally produced by, and occur only as constituents of the organs of plants and animals.

With oxygen, carbon forms two compounds—one, a neutral oxide, is called carbonic oxide; the other, carbon dioxide, CO_2, containing twice as much oxygen

in proportion to carbon, presents most of the characters of an acid oxide, and it forms with basic oxides saline compounds called carbonates, several of which occur naturally in great abundance and are of great technical importance. The hydrogen salt of carbon dioxide, H_2CO_3, or true carbonic acid, is not known. With sulphur, carbon forms a disulphide, CS_2, sulpho-carbonic acid, corresponding to the dioxide, but containing sulphur in place of oxygen. With nitrogen, it forms the pseudo-elementary substance, cyanogen, CN, and several other compounds which are closely related to cyanogen. The compounds of carbon with hydrogen are very numerous. As a class they are termed hydrocarbons.

There are several groups of hydrocarbons whose individual members differ from each other by CH_2, or by a multiple of CH_2. These are termed *homologous groups*, and they are named after the lowest members. Marsh gas and the several substances termed paraffins constitute a group of this kind. The following are the most important of such groups:—

The Marsh gas group.

Marsh gas, or hydride of methyl, CH_4 . . . . = $CH_3\}H\}$

Hydride of ethyl (dimethyl), C_2H_6 . . . . . = $C_2H_5\}H\}$

Hydride of propyl, C_3H_8 . . . . . = $C_3H_7\}H\}$ etc.

Higher homologues of this series are contained in petroleum, solar oil, etc.

The Ethylene group.

Olefiant gas, or ethylene	C_2H_4
Propylene	C_3H_6
Butylene	C_4H_8
Amylene	C_5H_{10} etc.

The Benzol group.

Benzol	C_6H_6
Toluol	C_7H_8
Xylol	C_8H_{10}
Cumol	C_9H_{12}
Cymol	$C_{10}H_{14}$

There are many hydrocarbons, which are totally distinct substances, but have exactly the same percentage composition; as, for instance, olefiant gas (ethylene), propylene, butylene, amylene, etc., but these substances are essentially different in their physical and chemical properties. They all contain 14·3 per cent. hydrogen and 85·7 per cent. carbon; but the molecules of these compounds require to be represented by different formulæ, though the proportions of hydrogen and carbon are the same in all.

A few of the hydrocarbon compounds are gaseous at the ordinary temperature: the greater number are liquid; such as, oil of turpentine, benzol, naphtha, etc.; or solid, like naphthalin, and some of the hydrocarbons of the paraffin series.

Although the number of hydrocarbons is extraordinarily great, only one of them has been obtained by the direct combination of hydrogen with carbon. This substance is acetylene, C_2H_2, which is formed when the electric arc is allowed to play for some time between two carbon electrodes in an atmosphere of hydrogen.

The substances which have the same composition as oil of turpentine, $C_{10}H_{16}$, constitute an important group of hydrocarbons.

The marsh gas series, hydride of ethyl, hydride of propyl, etc., are isomeric with the radicals of the alcohols. So far as industrial art is concerned, the most important member of the ethylene series is olefiant gas. The other members, propylene, butylene, etc., are formed together with olefiant gas in the destructive distillation of various organic substances for the manufacture of gas for purposes of illumination, and they exert considerable influence upon its illuminating power.

The hydrocarbons of the benzol series are formed in the destructive distillation of coal, as in the manufacture of coal-gas. They are found in the tar; from which material they are obtained by distillation. Benzol and toluol especially have now attained a great value, owing to their being the source from which aniline colours are prepared. Cymol is contained in the volatile oil of cumin.

Naphthalin and anthracene, $C_{14}H_{10}$, are likewise products of the destructive distillation of coal, that have also recently been made use of in the preparation of colouring materials.

Finally, the hydrocarbon termed acetylene, having a composition represented by the formula C_2H_2, occurs in coal-gas; and as it burns with a very bright flame, it also exerts an influence upon the illuminating power of the gas. Its presence in coal-gas can easily be detected by passing a stream of the gas through an ammoniacal solution of cuprous chloride. A reddish-brown precipitate is formed, consisting of a compound of acetylene with copper, $2(C_2HCu_2)O$, and possessing the property of exploding when dried and heated.

The carbon compounds that occur naturally as constituents of plants and animals, are much more numerous than those of any other elementary substance, and by various kinds of chemical alteration, a still greater number of derivative products may be obtained from them.

These organic substances are generally characterised by containing only carbon, hydrogen, oxygen and nitrogen; but their constitution is much more complex than that of other carbon compounds. In many cases, this circumstance is due to the fact that certain portions of the molecules of these substances present the characters of elementary substances, inasmuch as they perform the same functions as metals, or chlorine, sulphur, etc., in the compounds that are termed inorganic, just in the same way that in ammoniacal salts the group NH_4 acts the part of a metal. Thus, for instance, ordinary wine alcohol consists of carbon, hydrogen, and oxygen, C_2H_6O, and the composition of its molecule is represented by the formula $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$, as being analogous to that of the molecule of water H_2O, with the difference that the place of one atomic proportion of hydrogen is occupied by the group C_2H_5, which is termed ethyl or the radicle of wine alcohol, and this pseudo-elementary substance is capable of forming compounds with chlorine, iodine, etc., that are analogous to the corresponding compounds of metals. There are several other substances similar in this respect to ordinary wine alcohol, and they constitute a class of carbon compounds which are on that account termed alcohols. The compounds of alcohol radicles with oxygen represented by ordinary ether $C_4H_{10}O$ are in like manner analogous to water, both atomic proportions of hydrogen being replaced by ethyl, as in potassium oxide they are replaced by potassium, as shown by the following formulæ:

Ethyl oxide	Water	Potassium oxide
$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}K\\K\end{matrix}\right\}O$

The ethers constitute a very numerous class of substances which differ in character according to the nature of the alcohol radicles contained in them.

Several other classes of carbon compounds of a similar nature are designated by general terms, such as aldehydes, ketones, etc., which indicate resemblance to the particular representative substances that were originally known by these names, but have since become types of classes, as in the case of the aldehyde obtained from ordinary alcohol, and thus named because it was considered to be alcohol dehydrogenised.

The organic acids constitute another important class of carbon compounds, containing radicles, which are, in this case, analogous to the acid oxides of sulphur, phosphorus, etc. Acetic acid, for instance, $C_2H_4O_2$, is represented as containing a monobasic acid radicle C_2H_3O, called acetyl, corresponding to nitric oxide, in nitrates and the composition of the molecules of hydrogen acetate, or acetic acid, and of acetates, is represented, in conformity with that of the molecule of water, by the following formulæ:

Acetic acid	Potassium acetate	Water	Nitric acid
$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$

Oxalic acid and oxalates are represented in a similar manner as compounds containing the dibasic acid radicle C_2O_2, and corresponding to the double molecule of water and to sulphuric acid, as in the following formulæ:

Oxalic acid	Potassium oxalate	Water	Sulphuric acid
$\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_2O_2\\K_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$

Another class of carbon compounds, comprising many substances of great utility, is that of the alkaloids, such as quinine, morphia, strychnine, etc. These substances all contain nitrogen, and their constitution is very complex, but in general they present great analogy with ammonia and those derivatives of ammonia which contain alcohol radicles in the place of one or more atomic proportions of the hydrogen in ammonia.

The substances which resemble starch, sugar, etc., in containing carbon combined with hydrogen and oxygen in the same proportions as in water, and on that

account are termed carbohydrates, form an important class of carbon compounds. Their constitution is in many cases very complex, and the mode of representing it has not yet been assimilated to that of more simple compounds.

Lastly, the substances corresponding to albumen, casein, gelatin, etc., constitute another class of carbon compounds which are remarkable for containing nitrogen and sulphur, in addition to the usual elementary constituents of organic substances. The percentage composition of all these substances varies very little, but scarcely anything is known of their chemical constitution, beyond the fact that it is probably very complex.

The substances belonging to these different classes of carbon compounds which require to be treated of in this work, as being of interest from an industrial point of view, will be described subsequently either as general constituents of plants, etc., or in connection with the materials from which they are usually derived.

CARBONIC DIOXIDE.

Formula CO_2. Molecular Weight 44.

History.—This substance—commonly called carbonic acid—has been known for a very long time, although Van Helmont was the first to distinguish this gas definitely from others. Its true composition was first ascertained by Lavoisier.

Occurrence.—The natural sources of carbonic acid are very numerous, some of them furnishing enormous quantities; and, as has been mentioned in treating of the atmosphere, this is the reason that the amount of the carbonic acid in atmospheric air (about 0·04 per cent.), does not diminish, although it is constantly being consumed by plants. The respiration of animals is one of the principal sources of carbonic acid: it is also produced in a large number of processes of combustion, occurring either naturally or as the result of the industrial activity of man; as for instance, in the combustion of fuel, and in the various contrivances for the purpose of illumination, etc. In nearly all processes of fermentation, in every process of decay and putrefaction, carbonic acid is a product of the decomposition. Large quantities of carbonic acid are further poured into the atmosphere from active volcanoes; and sometimes, indeed, so abundantly that there is not time for it to diffuse itself equally into the surrounding air; and, owing to the great density of the gas, it flows, like a stream of lava, down the sides of the volcanoes, accumulating sometimes in hollows on their sides. On this account, it is often dangerous to pass through such places, in the neighbourhood of volcanoes. At other parts of the earth also, large quantities of carbonic acid are often met with, issuing from crevices and fissures, as for instance in the 'Dog's Grotto,' in the neighbourhood of Naples, at a few places near Trèves, and other parts of the Rhine district, as well as at Eger, Pyrmont, etc. A great quantity of carbonic acid is also discharged from the water of mineral springs. As already mentioned, the water of these springs has been saturated with carbonic acid at great depths, and under considerable pressure; but as the gas cannot be retained in solution at the ordinary pressure of the atmosphere, it is consequently given off when the water comes to the surface.

Though the quantity of carbonic acid existing in the free state is very great, it is far exceeded by that which occurs chemically, combined principally in the state of carbonates, as limestone, chalk, marble, dolomite, and magnesite, etc.

Composition.—Carbonic acid contains nearly one-fourth its weight of carbon: the normal volume of the oxygen it contains is equal to the volume of gas itself, and the gaseous volume of the carbon it contains is assumed to be half that of the oxygen, the combination being attended with a condensation of one-third the joint volumes of the constituents in the free state. It is therefore a compound of one atomic proportion of carbon with two atomic proportions of oxygen, and its composition is represented by the formula CO_2.

Characters.—Carbonic acid is at the ordinary temperature a colourless gas, possessing a very slight smell. It is not combustible, nor does it under ordinary conditions support the combustion of other bodies: neither is it a supporter of respiration, and hence it is that animals are suffocated in an atmosphere of the gas. It is, however, very different from carbonic oxide in its action upon the animal organism, for while carbonic oxide is positively poisonous, as is evident from the fact that air containing only a small amount of it causes death; carbonic acid may be inhaled in comparatively large quantities, without the slightest harm.

Carbonic acid gas is moderately soluble in water; at a temperature of 15° C. water

dissolves about its own volume (1·002 vol.), and at 0° under a barometric pressure of 760 mm. it dissolves 1·797 times its volume of the gas. As in the case of every other gas in respect to solubility, carbonic acid dissolves in water in larger proportion when the pressure is increased. Hence it is that the water of a spring, which has been saturated with carbonic acid at a great depth below the earth's surface, and under great pressure, gives off this gas upon coming to the surface of the earth. The same thing happens with various other liquids, such as champagne, soda water, etc., which are saturated with carbonic acid under considerable pressure, and give off the gas with effervescence when the pressure is removed.

Carbonic acid may be condensed to a colourless liquid by cooling it to a temperature of 0° under a pressure of 36 atmospheres. When the liquid is allowed to evaporate in the air, such an intense degree of cold is produced that a large portion becomes solid. Solid carbonic acid is a white, snow-like substance, which evaporates but slowly in the air, and melts at −57°.

The density of gaseous carbonic acid is 22 as compared with hydrogen; and its specific gravity relatively to air is 1·529; the specific gravity of the liquid acid is 0·830 as compared with water.

Preparation.—Carbonic acid is generally obtained by one of the three following methods: 1. Expulsion of the gas from its salts by means of strong acids. 2. Expulsion from its salts by heat. 3. By burning carbon or carbonaceous substances.

For the preparation of carbonic acid on a small scale, the first method is the most suitable. Calcium carbonate, a substance occurring very abundantly in various forms, as chalk, limestone, etc., is employed for this purpose, together with hydrochloric acid, the reaction that takes place giving rise to the formation of calcium chloride, while carbonic acid gas is set free.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

The calcium carbonate (marble or chalk being the most convenient), is placed in a Woulfe's bottle, fitted with a funnel and a delivery tube connected with a wash bottle containing a small quantity of water for the purpose of removing from the gas any hydrochloric acid that might be mechanically mixed with it. The gas may be collected either in a gasholder or over water by means of a pneumatic trough. After a quantity of water has been poured through the funnel into the generating bottle sufficient to cover the marble or chalk, hydrochloric acid is added in small quantities at a time through the funnel. Carbonic acid is then developed with strong effervescence, and is purified by passing through the water in the wash bottle.

Instead of this apparatus, one of a similar kind to that described on page 28, fig. 8, may be employed; the only difference being that the zinc ring is replaced by a perforated vessel containing marble, and resting upon a small glass tripod: hydrochloric acid being, of course, substituted for sulphuric acid.

Ordinary limestone may be used instead of marble or chalk in the preparation of carbonic acid; but this is not advisable on account of the impurity of the gas thus produced. Magnesite, a mineral consisting of magnesium carbonate, is very suitable as a source of carbonic acid, the gas obtained from it being very pure.

The second method of preparing carbonic acid, by the action of heat upon its salts, is not suitable for operations on a small scale. This process takes place in lime burning: the limestone, a substance occurring very abundantly, being converted by strong heat into calcium oxide (burnt lime), and carbonic acid:

$$CaCO_3 = CaO + CO_2$$

The carbonic acid produced in this process has of late been collected and made use of for various purposes.

The third method of obtaining carbonic acid, like the one just described, is only adapted for producing the gas on a large scale. It consists either in burning charcoal or coke in a special apparatus, with the sole object of obtaining carbonic acid, or as is sometimes the case obtaining the carbonic acid as a by-product of the ordinary combustion of fuel, by collecting the waste gases from furnaces. (*Vide* 'Sugar Manufacture.')

Carbonic acid may also be obtained as a by-product in alcoholic fermentation; sugar being in this case resolved into alcohol and carbonic acid; according to the equation:

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$$

Further, carbonic acid is produced in a number of chemical processes; by heating charcoal with concentrated sulphuric or nitric acid; also when any organic substance is melted with nitre or some other powerful oxidising agent; in the combustion of carbonic oxide, and in every process of putrefaction and decay, etc.

Uses.—Carbonic acid is very extensively employed in manufacturing industry. It is made use of in the preparation of artificial aërated water, and other liquids con-

taining carbonic acid. It is largely used for separating lime from the juice of the sugar-cane, the lime being for the most part precipitated as carbonate, by passing a stream of the gas into the heated juice.

Further, carbonic acid plays an important part in bread making; the gas being formed in the fermentation of the dough, and remaining dissolved, until the dough is heated in the operation of baking; when it expands and converts the dough into a spongy porous mass. In the fermentation of dough, a considerable quantity of material is lost in the shape of products of fermentation (alcohol and carbonic acid), and it has therefore, been attempted to produce the carbonic acid in the dough by artificial additions (Liebig bread, etc.) A process of the kind, which has been carried out on a large scale in London and other places by Dr. Dauglish, consists in charging water with carbonic acid, prepared either by the action of dilute sulphuric acid, or heat upon chalk, and mixing this carbonic acid water with flour under pressure. The resulting dough which becomes vesicular on the removal of the pressure, is divided into loaves and baked (*vide* article 'Bread'). The production of carbonic acid by the combustion of carbon compounds affords a means of analysing such substances. The carbon is converted by combustion into carbonic acid, which is collected in an apparatus containing caustic potash. From the difference between the weight of the apparatus, before and after the combustion, it is easy to ascertain the amount of carbon contained in the substance operated upon.

Attention has already been drawn (page 24) to the importance of carbonic acid in the nutrition of plants. Many other effects are referrible to the presence of carbonic acid in the atmosphere; for instance, the setting of mortar is due to the combination of carbonic acid with the lime of the mortar and the formation of calcium carbonate.

Compounds.—The important class of saline substances known as carbonates contain the elements of carbon dioxide combined with basic oxides. Carbonates are generally represented as compounds of the dibasic acid oxide CO_3 with metals. Thus the molecule of neutral calcium carbonate—chalk or marble—containing $CO_2 + CaO$ is represented by the formula $CaCO_3$. Besides the neutral carbonates, there are a great number of carbonates containing excess of base, and the carbonates of monovalent metals form acid salts by the replacement of one atomic proportion of metal by hydrogen. Thus, for instance, ordinary sodium carbonate, Na_2CO_3, by combining with water and an additional proportion of carbon dioxide, furnishes two molecules of the salt, $NaHCO_3$, commonly called bicarbonate. With the exception of the carbonates of the alkalies and of ammonia, the carbonates are insoluble or only sparingly soluble in water. Ammonium carbonate is the only one soluble in alcohol. Most carbonates are decomposed by heat, some at a comparatively low temperature, like lead or zinc carbonate, giving off carbon dioxide and leaving lead or zinc oxides: calcium carbonate requires a greater heat, and the alkaline carbonates are scarcely at all decomposed by heat alone. When heated in contact with an atmosphere of water vapour carbonates are more readily decomposed. Carbonates are decomposed by the greater number of acids in the presence of water, and the liberation of the gas from the liquid gives rise to the phenomenon of effervescence. Carbonates are also decomposed in a similar manner by heating them with fixed acids, such as silicic, and when heated in contact with carbon they are decomposed with evolution of carbonic oxide.

The compound of carbon dioxide with ammonia, formed when the dry gases are mixed, and sometimes called anhydrous ammonia carbonate, is the ammonium salt of an acid called carbamic acid, HNH_2CO_2, the composition of the salt being represented by the formula $NH_4NH_2CO_2$. This substance is contained in the ordinary ammonia carbonate of commerce. It is a white flocculent mass readily soluble in water, yielding, by combination with the elements of water, a solution of neutral ammonium carbonate.

Artificial Aerated or Mineral Waters.

The various kinds of effervescent water known as soda water and seltzer water are prepared from ordinary potable water, with or without addition of saline substances, by charging it with carbonic acid under a pressure of from 4 to 6 atmospheres. Consequently, good soda water or seltzer water should contain from 4 to 6 times as much carbonic acid as well aerated potable water contains under ordinary conditions. It is evident that water thus charged with carbonic acid under pressure requires to be kept in well-corked bottles. Should the cork fit imperfectly, the carbonic acid gradually escapes, and when the cork is removed altogether, the gas is given off with brisk effervescence.

The material used in the preparation of the carbonic acid is generally limestone or marble, which is decomposed with hydrochloric acid. Sometimes chalk or magnesite is employed, and decomposed by means of sulphuric acid. For the preparation of

carbonic acid on a small scale, double sodium carbonate is very suitable, as it yields very pure carbonic acid, free from the bituminous and earthy smell which carbonic acid prepared from lime, chalk, etc., sometimes possesses.

The use of carbonic acid produced by fermentation has been recommended for the preparation of effervescing beverages by MM. Gressler and Wachler. Many different forms of apparatus are in use for preparing carbonic acid water, one of the most common of which is represented by fig. 24.

This apparatus consists essentially of two parts, viz., the apparatus in which the carbonic acid is generated (from A to E), and that in which water is saturated with the gas (from E′ to H).

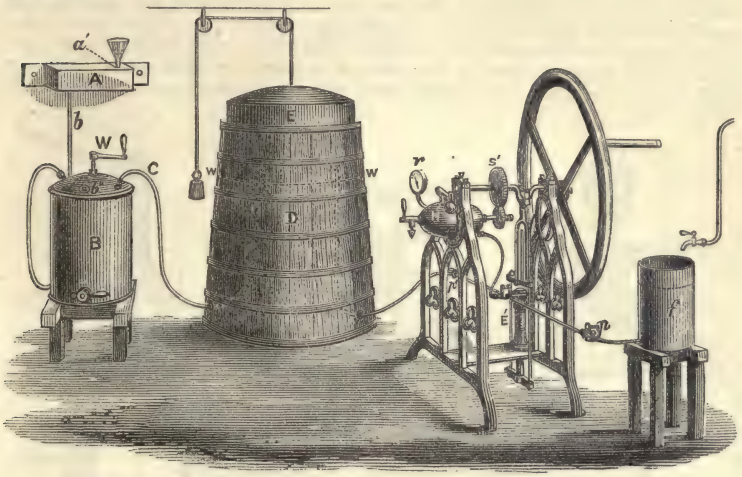


Fig. 24.

The vessel (B) in which the gas is generated is made of lead; the opening (b''), admitting of being closed with a screw plug, is for putting in the carbonate to be decomposed. and the pipe (b) is for supplying acid, which is poured into the leaden vessel (A) through the opening (a') at the top. For the purpose of accelerating the evolution of carbonic acid, a stirrer is fitted inside, and when set in motion by means of the crank (W), it has the effect of distributing the acid flowing in through the pipe (b), and bringing it into more intimate contact with the pieces of chalk or marble in the vessel B.

The chemical change that takes place in B is very simple, the carbonic acid of the magnesium or calcium carbonate being expelled by the stronger mineral acid used. It is represented by the following equations:

With sulphuric acid

$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2.$$

With hydrochloric acid

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

The carbonic acid evolved in B escapes through the tube (C), which passes into the wash vessel (D) made of wood and lined with lead. This vessel is filled with water up to the level (WW), and the gas delivery tube (C), extending above the water level, turns down again so as to dip into the water. In this way the gas is made to pass through the water, which serves to retain particles of mineral acid or salt carried over by it. The washed gas then collects in the gas-holder (E), consisting of a sheet iron or copper bell, which rises and falls in the vessel in which it hangs, according to the quantity of carbonic acid present. The height of the bell is, therefore, an indication by which the supply of acid to the generator (B) may be regulated.

The solution of the gas in water is effected in a strong copper cylinder (H) lined with tin and fitted with a pressure gauge (r), a safety valve, and a tap for drawing off the aerated water for bottling. This cylinder (H) is connected by means of a tube with the pump (E′), by which gas is drawn out of the gas-holder, and at the same time water is drawn from the small cistern (f), and both are then forced into the cylinder (H) until the pressure indicated by the gauge (r) shows that the water is sufficiently charged with gas. The flow of water and of carbonic acid into the condenser admits

of being regulated by the cocks (p and p'), so that water, rich or poor in carbonic acid, may be obtained at pleasure, and the saturation of the water with carbonic acid is aided by a stirrer fitted inside the cylinder, and turned by the toothed wheel (s') upon the shaft of the fly wheel. In warm weather it is sometimes necessary to cool the water before charging it with gas.

This apparatus can be worked either by manual labour or by steam power, and when once the cylinder is charged with sufficiently aerated water, it works continuously, when the supply of water and gas to the cylinder (H) is regulated by means of the cocks (p and p'), according to the rate at which the aerated water is bottled off.

In the apparatus represented by fig. 25, carbonic acid is generated in the cylindrical vessel (G) which contains the calcium carbonate, and is fitted with a safety valve (S) and with an agitator worked by the handle (H). Acid is supplied from the reservoir (A) by opening a valve worked by the handle (V), and when a sufficient quantity has been run in, the valve is again closed. The water to be charged with carbonic acid is contained in the cylinder (C), which is also fitted with an agitator worked by the handle

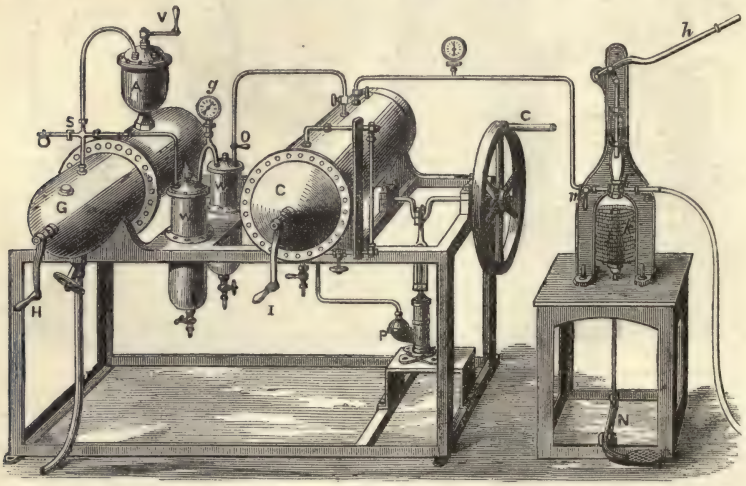


FIG. 25.

(I), and between this cylinder and the generator (G) there are two small cylinders (W W') containing water for washing the carbonic acid gas. The small cylinders or washers are connected with the cylinders (C and G) in such a way that when the outlet tap (O), by which the gas is allowed to escape from the generator, is opened, the escaping gas passes successively through W and W' before entering C. In this arrangement the pressure exerted by the evolution of carbonic acid gas in G is made to do the work of forcing the gas into solution in the cylinder C, which is fitted with a pressure gauge (g) for indicating when the water is sufficiently charged with gas and ready for bottling. When this result has been produced, the communication between C and G is shut off and the water is bottled in the usual way.

In order to carry on work continuously with this apparatus, two cylinders like C are fitted side by side with connecting pipes and stop valves arranged in such a way that either one can be placed in communination with the generator. As soon as the water in one cylinder is charged with gas, the valves between it and the generator are closed, and those between the other cylinder and the generator are opened. While the second cylinder is being charged with gas, the water in the first cylinder is bottled off, and so on alternately. When the cylinders are emptied, they are charged with water again by means of the pump (P) worked by the crank (c).

Bottling.—In filling bottles with water highly charged with carbonic acid, each bottle (k) is set in a semicylindrical frame, so as to protect the workmen from splinters of glass should the bottle burst during the operation. The mouth of the bottle is pressed up by the lever (N) against a small caoutchouc plate with a hole in the middle, which is fitted into a metal collar communicating on one side with the cock (m) and on the other side with a valve (n) capable of being adjusted by a spring. In the cavity above the caoutchouc plate is fixed at (l) a cork, which has been previously softened in water. On opening the cock (m) the aerated water passes into the bottle in proportion as the air escapes from the valve (n).

Directly a bottle is filled up to the neck with aerated water, the cock (*m*) is closed, and the cork (*l*) pressed by means of a plunger worked by the lever (*h*) into the neck of the bottle.

The bottle is removed by lowering the lever (N). It is then placed on a table, and the cork held fast by means of a couple of bent iron rods, while a workman secures it with wire or string.

It is advisable to test the bottles before filling by exposing them to a pressure of from 10–16 atmospheres, so as to avoid injury to the workman during the filling. The condenser in which the water is saturated with carbonic acid is tested before use by exposing it to a pressure of 20 atmospheres. The testing is without danger, water being used, and water has such very little elasticity that, even if a vessel containing it under great pressure should happen to spring, the pieces of the broken vessel are not scattered about with any great violence.

It is evident that the apparatus above described for preparing aerated water admits of being employed in the preparation of all effervescing beverages: such as artificial sparkling wines, lemonade, etc., it being only necessary to fill the compressor with the liquid required.

CARBONIC OXIDE.

Formula CO. Molecular Weight 28.

Composition.—Carbonic oxide has the composition represented by the formula CO: it was discovered by Priestley in 1799.

Characters.—Carbonic oxide is a colourless, tasteless, and inodorous gas, that has at present resisted all attempts to condense it to the liquid state. Its specific gravity is 0·968. Carbonic oxide is only slightly soluble in water; 100 volumes of water at 0° absorbing only about 3·3 volumes of the gas; it is, on the contrary, easily soluble in a solution of cuprous chloride. Carbonic oxide is combustible, and it burns with a beautiful blue flame, which is very characteristic. The product of its combustion is carbonic acid.

Carbonic oxide does not possess the characters either of an acid or of a base; it is chemically an indifferent, or neutral, body. At high temperatures carbonic oxide acts as a powerful reducing agent, abstracting oxygen from most metallic oxides, when brought into contact with them at a red heat.

When respired, carbonic oxide acts as a powerful poison, probably by robbing the blood of oxygen. Its poisonous action upon the animal organism is so powerful, that small animals die in a very short time when placed in an atmosphere containing only 1 per cent. of carbonic oxide gas. In still smaller quantities, it causes an unpleasant feeling; headache, dizziness, and even syncope.

The fatal effect of burning charcoal in a closed room, with insufficient ventilation, is owing to the formation of carbonic oxide. It is supposed that in this case, carbonic oxide is not a direct product of combustion; but that here, as in every other case of combustion, whether the access of air be limited or not, carbon probably burns in the first instance to carbonic acid; and that this gas is afterwards reduced to carbonic oxide by contact with the red-hot fuel.

Preparation.—Carbonic oxide is easily obtained by passing carbonic acid gas through a tube filled with pieces of charcoal and heated to redness. Under these conditions, the carbonic acid combines with an additional proportion of carbon, and is thus converted into carbonic oxide according to the following equation

$$\begin{array}{ccccc} CO_2 & + & C & = & 2\,CO \\ 44 & & 12 & & 56 \end{array}$$

Carbonic oxide can also be prepared by heating a mixture of finely powdered calcium carbonate with one-sixth of its weight of charcoal powder in an iron retort. At a red heat, the calcium carbonate gives off its carbonic acid, and this reacts with the charcoal present in the manner above described.

The most convenient method, however, of preparing carbonic oxide is to heat oxalic acid, or an oxalate with strong sulphuric acid. For this purpose, either crude oxalic acid, or salt of sorrel, is placed in a capacious flask, covered with seven or eight times its weight of concentrated sulphuric acid, and the mixture heated. Carbonic oxide is then evolved, mixed with some carbonic acid, the mass frothing considerably. On this account, the flask should not be more than half filled. The formation of carbonic oxide in this case depends upon the fact, that when the sulphuric acid abstracts either from the oxalic acid the whole of its water, or from the oxalate the

whole of its base, the oxalic anhydride, thus set free, is resolved into carbonic oxide and carbonic acid:

$$\underset{90}{C_2H_2O_4} = \underset{18}{H_2O} + \underset{44}{CO_2} + \underset{28}{CO}$$

A method, very much to be recommended for the production of carbonic oxide, consists in heating in a glass flask a mixture of yellow prussiate of potash (potassium ferrocyanide) with nine times its weight of concentrated sulphuric acid.

In all the processes above described for the preparation of carbonic oxide, the gas is accompanied by carbonic acid. To remove this, the gas must be passed through milk of lime or a solution of caustic potash contained in two or three Woulfe's bottles.

MARSH GAS.

Formula CH_4. Molecular Weight 16.

Occurrence.—Marsh gas is formed in considerable quantities in marshes and stagnant pools, at the bottom of which vegetable remains are under going decay, the decomposition of such materials under water, without access of air, being favourable to the production of the gas. The gas often observed rising to the surface of stagnant water, more especially if the bottom be stirred with a stick, consists chiefly of marsh gas, mixed with nitrogen and carbonic acid. In order to collect the gas, it is only necessary to invert a bottle filled with water over the spot where the gas is issuing, and to conduct the bubbles into the bottle by means of a funnel.

In certain districts, marsh gas is found escaping from the surface of the earth. Such gaseous exhalations occur in Italy, on the northern slopes of the Apennines, at Velleja, Pietramala, Barigazzo, etc.; in France, at St.-Barthélemy; in this country in the neighbourhood of Lancaster and Brosely, as well as in Persia and in Mexico. The gas generally issues from the ground, accompanied by mud containing common salt; whence those springs have obtained the name of mud volcanoes. It does not appear probable that these springs are always volcanic, since they often occur in districts far removed from volcanoes. The occurrence of the gas together with mud in such springs, probably indicates that it has been formed by the decay of plant remains.

Marsh gas occurs in very large quantities in coal-mines, and is on this account sometimes called pit gas. Being confined under great pressure in the interstitial spaces of the coal, it rushes into the passages of the mines when such interstitial spaces are opened in course of working a seam of coal. Here it comes in contact with air, forming an explosive mixture, which often causes the greatest devastation, if the miners incautiously approach with a naked light. Miners term the gas fire damp.

The reason why these explosions are so dangerous, is the enormous expansion of the gases that takes place suddenly owing to the heat developed: by the violent concussion thus caused, the workmen are hurled from the spot with great violence, or the walls and roof of the passages are shattered and the mine choked up.

Characters.—Marsh gas, or light carburetted hydrogen, is a colourless, tasteless gas, very sparingly soluble in water: it has not as yet been condensed to a liquid, either by the application of cold or pressure. As compared with hydrogen its density is 8, and its specific gravity in relation to air is 0·554.

When respired, marsh gas does not act as a direct poison, but it is not a supporter of respiration. It is combustible, and burns with a yellowish flame of feeble illuminating power, the products of combustion being water and carbonic acid. A mixture of this gas with ten times its volume of air, or with twice its volume of oxygen, explodes with great violence when brought into contact with a flame.

Composition.—This substance contains three-fourths its weight of carbon, and twice its own volume of hydrogen.

Preparation.—In order to prepare pure marsh gas, the best method is that of heating together a mixture of sodium acetate and calcium hydrate, collecting the gas evolved in a gas-holder (fig. 3, p. 20), or by means of a pneumatic trough over water (fig. 1, p. 18). The residue in the retort after the operation is over, consists of the carbonates of sodium and calcium.

Circulation of air in coal mines.—One plan of preventing explosions consists in maintaining a rapid change of the air in coal-pits, by means of artificial ventilation. Even in coal-mines where fire damp is only occasionally met with a circulation of air is necessary, for the reason, that without due ventilation, the explosive gases gradually accumulate. For, though large quantities of fire damp seldom appear suddenly, there is in many coal-pits a continual evolution of marsh gas, which, when it has time to collect in any particular part of the pit, may easily give rise to an explosion.

Coal obtained from pits where fire damp is prevalent generally contains marsh gas in its cavities; this is shown by the fact that such coal explodes with a loud report when heated, and sometimes indeed spontaneously at the ordinary temperature. When coal is freshly taken from pits of this kind, it often gives off such a quantity of gas that it may be burnt at the mouths of the hutches in which the coal is brought up from the mine.

The arrangement for obtaining an artificial current of air is generally the following. Two air-shafts lead into the mine, and at the mouth of one of them is a furnace, with a chimney fifty or sixty feet high. This furnace is so connected with the shaft of the mine, that it can only obtain the necessary supply of air out of the shaft itself. This shaft being in communication with the galleries of the mine, the bad air is thus drawn from the mine and replaced by pure air which enters by the other air shaft.

In order to prevent the flame of the furnace from setting fire to inflammable gases in the pit, the ventilating tube connecting the furnace with the shaft is fitted with partitions of wire gauze, through which flame cannot pass.

The vicinity of fire damp is indicated to the miner by the flame of his lamp. The presence of a small quantity of fire damp in the air at a considerable distance from the explosive mixture, causes the flame to lengthen and burn with a blue colour, which increases in depth as the amount of fire damp in the air increases. If there is danger of an explosion, it is advisable for the workman to lie down flat upon the ground, for in that position, he offers less resistance, should an explosion take place.

Davy's Safety Lamp.—The problem of lighting coal-mines in such a manner, that the source of light should not cause the firing of inflammable gases, has been the object of many researches. Davy especially conducted a number of experiments with this end in view, and at last effected a solution of the problem. First of all, he experimented with phosphorescent substances, which after having been exposed to sunlight, possess an illuminating power in the dark, without evolving any perceptible heat. However, the light emitted by all such substances is too weak for lighting up a mine.

Davy next studied the degree of inflammability of various mixtures of marsh-gas and air; and upon setting light to them with a flame, he obtained the following results:—

Marsh gas	Air	
1 vol.	2 vols.	The mixture burns without detonation.
,,	3 ,,	,, ,,
,,	4 ,,	,, ,,
,,	6 ,,	The mixture burns with weak detonation.
,,	7 ,,	The mixture burns with stronger detonation.
,,	8 ,,	,, ,,
,,	9–10 ,,	The mixture burns again with weaker detonation.
,,	15 ,,	The mixture no longer ignites; the flame of a candle immersed in it lengthens.
,,	16–30 ,,	The mixture does not ignite; the lengthening of the candle-flame is less.

From these results, it is evident that a mixture of one volume of marsh gas and eight volumes of air is the most explosive. One volume of pure marsh gas would require ten volumes of air for the combustion of the whole of its carbon and hydrogen to carbonic acid and water.

Davy also found that a red-hot substance, such as a piece of red-hot charcoal, might be introduced into an explosive mixture of air and marsh gas without setting fire to it. Marsh gas is, therefore, less inflammable than carbonic oxide, olefiant gas, sulphuretted hydrogen, or pure hydrogen; all of which are set fire to when a piece of red-hot charcoal is brought in contact with them. Accordingly, since a mixture of marsh gas and air is not easily ignited, Davy conceived the idea of preventing explosions by cooling the flame. Experimenting with an explosive mixture of hydrogen and air, he found that, although it was more easily inflammable than one containing marsh gas, the flame did not extend through metallic tubes of very narrow aperture, nor even through very fine holes made in a piece of thin sheet metal. Eventually, he employed wire gauze, and found that it prevented flame from extending throughout the entire mass of an inflammable gas, by the cooling effect it produced, just like a metallic tube of small diameter, or a plate with fine holes.

Consequently, by using a lamp with the flame surrounded by wire gauze, so that the air necessary for combustion, as well as the products of combustion, can enter and escape only through the wire gauze, the firing of an inflammable gas surrounding the lamp is rendered impossible. The cooling effect of the wire gauze prevents the propagation of flame.

In the lamp used originally, and to a great extent even at the present time, a cylinder of wire gauze closed above was fixed round the flame in such a way that it rested on the oil vessel of the lamp. To prevent a miner being suddenly left in the dark from the flame of his lamp being extinguished by an atmosphere of marsh gas, Davy fitted his lamp with an arrangement by means of which, after the extinction of the flame the man would still have light enough to find his way back. This arrangement consisted of a spiral of platinum wire, surrounding the flame of the lamp and kept red hot by it. If the flame is extinguished by contact with marsh gas, the platinum spiral continues red hot, since the gas which comes in contact with it continues to burn slowly, and thus produces a feeble light.

The safety lamps made according to Davy's construction give only a feeble light, on account of the wire gauze through which it has to penetrate. The consequence of this is that, in order to obtain more light, the workmen often partially remove the wire gauze; and thus accidents have often occurred in spite of the safety lamps. On this account the construction of the lamps has been improved, so that greater illuminating effect, as well as greater safety, have been obtained.

Safety lamps give considerably more light when constructed as follows: The flame is surrounded by a globe or cylinder of thick glass; this glass is fitted into a double cylinder of wire gauze, closed above also with double wire gauze, through which the products of combustion escape, and air for the support of the flame enters the interior of the glass cylinder through a double wire gauze. By the use of double wire gauze, the inner one is protected by the outer from coal-dust, while the outer one is prevented by the inner one from becoming too hot.

The metal of which the wire gauze is made is not immaterial. If platinum wire be heated only moderately in an explosive mixture of marsh gas and air, it soon acquires such a temperature that it is capable of causing the explosion of the gas. This is also the case with wire made of silver or gold; on which account these metals are not suitable as material for the wire gauze of safety lamps; although, on the other hand, owing to their not becoming oxidised when heated, they would be in that respect very suitable for the purpose. Davy's experiments in this direction showed that the wire gauze is best made either of copper, brass, or iron wire.

OLEFIANT GAS.

Formula C_2H_4. Molecular Weight 28.

Characters.—Olefiant gas, also called heavy carburetted hydrogen, or ethylene, is at the ordinary temperature a colourless gas, which under strong pressure at $-110°$ is condensed to a colourless liquid. It possesses a peculiar ethereal smell; burns with a luminous flame; is very sparingly soluble in water, but is rapidly absorbed by concentrated sulphuric acid. A saturated solution of olefiant gas in sulphuric acid when diluted with water yields alcohol, which may be distilled from the mixture.

Olefiant gas is considerably denser than marsh gas; as compared with hydrogen, its density is 14, and relatively to air its specific gravity is 0·9784.

When passed through a tube heated to redness olefiant gas is decomposed, yielding marsh gas and hydrogen together with carbon, which is deposited on the sides of the tube. This property of olefiant gas must be considered in the manufacture of coal-gas, the lighting effect of which is chiefly due to the ethylene it contains.

A mixture of ethylene with about fifteen times its volume of air explodes upon contact with the electric spark, or other flame, yielding water and carbonic acid.

Olefiant gas enters into direct combination with concentrated sulphuric acid. As marsh gas does not combine with sulphuric acid, this reaction serves for the separation of the two gases. If olefiant gas be brought into contact with chlorine in the dark, it forms with it an oily liquid, having a composition corresponding to the formula $C_2H_4Cl_2$, which, from its discovery by four Dutch chemists, has been called Dutch liquid; and from the oily appearance of this product, the gas itself received its name 'olefiant.' If chlorine be allowed to act upon olefiant gas in the sunlight, there is formed chiefly a product represented by the formula $C_2H_3Cl_3$.

Preparation.—Olefiant gas may be prepared on a small scale, by heating together, in a retort or flask, a mixture of alcohol and from four to five times its weight of concentrated sulphuric acid. This mixture froths considerably when heated and especially towards the end of the operation; therefore the generating vessel should not be more than half filled. The frothing may also be prevented by mixing the acid and alcohol with enough sand to form a pasty mass. The gas evolved upon the application of heat to this mixture is very impure, containing carbonic and sul-

phuric acids, alcohol and ether; to remove which the gas is passed through two Woulfe's bottles, containing caustic soda, and through a third, containing some concentrated sulphuric acid. After having undergone this process of purification, the gas may be collected over water, or in a gasometer.

Taking the empirical formula of alcohol as C_2H_6O, it is evident that it can be resolved into C_2H_4,H_2O, and that accordingly alcohol contains the elements of olefiant gas and of water. If pure alcohol be heated to 170°–180°, together with concentrated sulphuric acid, the dehydrating affinity of the latter causes the decomposition of the alcohol into water, which combines with the sulphuric acid, and into olefiant gas which escapes.

When wood, coal, or resins and other allied organic bodies are heated with exclusion of air, olefiant gas is formed together with various other products. A very extensive application is made of this mode of formation of olefiant gas, in the manufacture of illuminating gas, in which ethylene is the most important product. (*Vide* 'Gas Manufacture.')

Uses.—Olefiant gas, mixed with allied hydrocarbons and other gases, is a constituent of the different kinds of illuminating gases. Besides this, attempts have been made to prepare alcohol from olefiant gas, or from mixtures of it with the other hydrocarbons obtained by destructive distillation.

CYANOGEN.

Formula CN. Molecular Weight 26

History.—This substance, which is interesting chiefly on account of its pseudo-elementary character, was first obtained in a separate state by Gay-Lussac in 1815, but many of its compounds had long been known as articles of technical utility. On account of the blue colour of its compound with iron, known as Prussian blue, it was named from *κυανός* blue, and *γεννάω* to produce.

Composition.—Cyanogen contains nearly half its weight of carbon and its own volume of nitrogen, and assuming the normal gaseous volume of the carbon it contains to be equal to that of the nitrogen, the combination is attended with a condensation amounting to one-half the total volume of the constituents.

Characters.—Cyanogen is a colourless gas of peculiar odour. Its density is 13 as compared with that of hydrogen, and its specific gravity in relation to air is 1·806; by cooling or compression it condenses readily to a liquid of 0·866 specific gravity as compared with water, and by further cooling it solidifies. The gas dissolves in one-fourth its volume of water and still more copiously in alcohol. It is very poisonous. Cyanogen is combustible, and burns with a blue flame yielding carbon dioxide and nitrogen:

$$CN + 2O = CO_2 + N.$$

One of the most remarkable characteristics of cyanogen is the analogy between it and chlorine in its chemical relations as a pseudo-elementary substance, and on this account it is often represented by the symbol Cy; it combines directly with metals, forming saline compounds, called cyanides, which are analogous to the chlorides. The hydrogen compound corresponding to hydrochloric acid, and known as hydrocyanic or prussic acid, cannot be formed directly, but is readily obtained by the action of strong acids upon the metallic cyanides.

Many of the cyanides combine with each other, forming a large number of compounds, which may be regarded as double cyanides, or as containing a still more complex molecular group than cyanogen, that also acts, like it, the part of an elementary substance, as in the ferrocyanides, which contain the elements of ferrous cyanide $FeCy_2$ and of 4 molecules of the cyanide of a univalent element or radicle, as in the case of the salt called yellow potassium prussiate or potassium ferrocyanide, the formula of which is $K_4Fe''Cy_6 = 4KCy + Fe''Cy_2$. Red potassium prussiate $K_6Fe_2'''Cy_{12}$ represents another class of compound cyanides termed ferricyanides, and there are several analogous series of compounds containing cobalt or other metals in the place of the iron of ferrocyanides and ferricyanides. These substances are regarded as containing compound radicles termed ferrocyanogen, ferricyanogen, cobaltocyanogen, etc., which are, like cyanogen, analogous to chlorine and act the part of pseudo-elementary substances. Two other cyanogen compounds corresponding respectively to water and sulphuretted hydrogen, in which half the hydrogen has been replaced by cyanogen, possess the characters of acids, viz. cyanic acid HCyO and sulphocyanic acid $HCyS_2$, and they are the representatives of two series of salts called cyanates and sulphocyanates, some of which are of technical importance.

POTASSIUM CYANIDE.

Formula KCy. Molecular Weight 65·1.

Characters.—This substance is commonly met with in the state of a white opaque mass, which gives off the odour of hydrocyanic acid; it is deliquescent and very soluble in water, crystallises in transparent colourless cubes, and is extremely poisonous. It melts readily at a low red heat, and is volatilisable at a much higher temperature, apparently without decomposition.

Preparation.—Potassium cyanide is prepared by the action of heat on well-dried potassium ferrocyanide, the decomposition being represented by the following equation:

$$K_4C_6N_6Fe = 4KCN + FeC_2 + 2N.$$

Generally the ferrocyanide is mixed with potassium carbonate in order to prevent decomposition of part of the cyanogen, and to obtain a larger yield of cyanide; but in this case the product contains some potassium cyanate, as shown by the following equation:

$$K_4C_6N_6Fe + K_2CO_3 = 5KCN + KCNO + Fe + CO_2.$$

A mixture of anhydrous ferrocyanide with three-eighths of its weight of dry carbonate is thrown in successive small portions into a red-hot cast-iron crucible, and the heat maintained until the evolution of gas has nearly ceased and the melted mass becomes colourless. The crucible is then gradually withdrawn from the fire, and after its contents have been allowed to settle, the clear melted cyanide is poured out upon an iron slab.

Uses.—Potassium cyanide is largely used in electro-plating, in photography, and as a chemical reagent.

POTASSIUM FERROCYANIDE.

Formula K_4FeCy_6. Molecular Weight 368·4.

History.—This substance, commonly called yellow prussiate, was first prepared by Macquer about the middle of the eighteenth century, and is largely used in dyeing and calico-printing, as well as for the preparation of several other cyanogen compounds.

Potassium ferrocyanide may be regarded either as the potassium salt of a compound radicle, ferrocyanogen C_6N_6Fe, sometimes represented by the symbol Cfy, or as a double compound of potassium cyanide and ferrous cyanide. The crystallised salt contains water, and its composition is represented by the formula $K_4FeCy_6 + 3H_2O$.

Characters.—Potassium ferrocyanide crystallises in yellow transparent tables; it dissolves in 4 parts of cold water and in 2 parts of hot water. Heated to 100°, the salt gradually loses its water of crystallisation, and is converted into a white powder consisting of the anhydrous salt. At a red heat it decomposes, giving off nitrogen and leaving a mixture of potassium cyanide and iron carbide.

An aqueous solution of potassium ferrocyanide produces in solutions of ferric salts a dark blue precipitate called prussian blue; protosalts of iron yield with potassium ferrocyanide a bluish precipitate which by contact with the air is gradually converted into prussian blue. Solutions of copper salts yield with potassium ferrocyanide a dark reddish-brown precipitate.

Preparation.—On the large scale potassium ferrocyanide is prepared by adding nitrogenous organic substances, such as horn, feathers, dried blood, etc., to fused potassium carbonate, lixiviating the residual mass with water and bringing it into contact with a salt of iron. During the melting process potassium cyanide is formed from the potassium of the potash and the nitrogen and carbon of the organic substance, and that salt when brought into contact with iron in the lixiviation yields potassium ferrocyanide, according to the equation:

$$6KCy + Fe + 2H_2O = K_4FeCy_6 + 2KHO + H_2.$$

Since it has been observed that the iron vessels in which the mixture is melted are very much attacked, it is now usual to add iron in a fine state of division to the melted mass. By the reduction of potassium sulphate contained in the crude potash, potassium sulphide and a double sulphide of iron and potassium are produced, which dis-

solve on subsequent lixiviation of the mass, and the iron sulphide and potassium cyanide react upon one another, forming potassium ferrocyanide and potassium sulphide according to the following equation:

$$6KCy + FeS = K_4FeCy_6 + K_2S.$$

Some potassium sulphocyanide is also formed during the melting process, but it is decomposed by the iron, with the formation of iron sulphide and potassium cyanide. The destruction of the iron vessels, observed in cases where no iron was added to the melted mass, is therefore simply explained by the iron required for the above reactions having been taken from the sides of the iron vessels.

The great loss of nitrogen which takes place in the manufacture of potassium ferrocyanide is very disadvantageous. At the most only one-fourth of the nitrogen added in the form of animal substances is obtained in the form of potassium ferrocyanide, and the remaining three-fourths escaping for the greater part as free nitrogen, together with a small quantity of ammonia.

The potash used in the preparation of potassium ferrocyanide must be very pure, in order to avoid accumulation of foreign salts in the mother liquor. The organic substances are carbonised previously to being mixed with the fused potash, so as to get rid as far as possible of the sulphur they contain. The nitrogenous organic substances consist chiefly of animal refuse.

The proportion of organic substance required, as well as its value, depends upon the percentage of nitrogen it contains. The following table by Karmrodt gives the percentage of nitrogen in different kinds of animal refuse:—

	Amount of Nitrogen per cent.		Amount of Nitrogen per cent.
Horn	15 to 17	Hide clippings	4 to 5
Dried blood	15 „ 17	Old shoes	6 „ 7
Woollen rags	10 „ 16	Charcoal from horn according to the heat to which it has been subjected	2 „ 7
Sheep shearings	16 „ 17		
Calves-hair	15 „ 17	Charcoal from rags	2 „ 12
Bristles	9 „ 10		
Feathers	17		

The iron required in the preparation of yellow prussiate is employed as filings or turnings, or in some other finely divided state, the fine division being necessary so that the melted mass may act upon it more readily than upon the sides of the iron vessels.

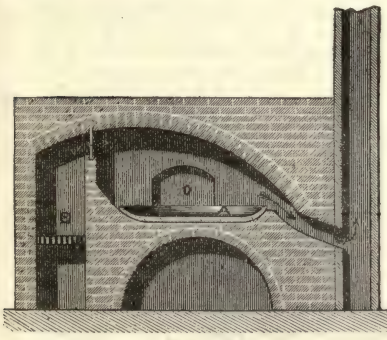


Fig. 26.

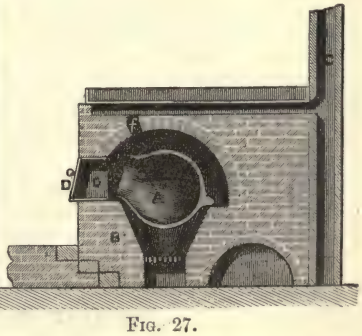


Fig. 27.

The melting vessels consist either of strong spherical or shallow cast-iron pans, which are set in the brickwork in such a way that the flame of a furnace can play round or over them, as shown in figs. 26 and 27. Great care must be taken that no air has access to the melting space, for in that case some organic substance would be burnt, and some of the potassium cyanide would be oxidised to cyanate. To prevent this, the combustion of the fuel must be so regulated that no excess of air passes with the flame into the melting space, but rather undecomposed carbonaceous gases. This is best effected by generating carburetted gas from the fuel in a special apparatus, and mixing it carefully with a sufficient quantity of air before it passes into the melting space.

The older form of apparatus, represented by fig. 27, consists of a spherical cast-iron pot (A) set in the furnace (B), so that the flame plays round it before escaping by the flue (*f*) into the chimney (C), and a space is left between the mouth of the iron pot and the arch of the furnace for the escape of volatile products. Opposite the mouth of the iron pot is an opening (*o*) in the wall of the furnace, capable of being closed by an iron door (D) and the materials used are thrown into the pot through this opening.

Reverberatory furnaces are sometimes employed, as shown by fig. 26. In this case the operation is conducted in a shallow iron pan (A), heated by the flame passing over it from the fire at B, and at *o* is the door for changing the pan.

The method of operating is as follows:—The potash (some few cwts. being taken) is first melted, and then the nitrogenous organic substance mixed with iron filings is gradually added. A strong evolution of gas takes place at first, blue flames of carbonic oxide are observed, while at the same time the organic substance dissolves and potassium cyanide is formed. After all the organic substance has been added, and the whole mass, which is termed the melt, has come to a state of tranquil fusion, it is ladled out into iron pans to cool.

The melted mass, when cold, is lixiviated, and for this purpose it is broken up into pieces about the size of an egg and thrown into iron lixiviating vessels. It is there covered with water, and the ley heated for a day to 70°—80° by passing steam into the lixivating vessel, the liquor being thus concentrated to a specific gravity of 1·16 to 1·22. During this operation the potassium cyanide dissolves, and reacts upon the iron and iron salts in the way previously described to form potassium ferrocyanide. After being allowed to clear, the liquor is drawn off and evaporated to a specific gravity of 1·27, when it yields crystals of potassium ferrocyanide upon cooling.

The mother liquor contains a considerable quantity of undecomposed potassium carbonate. It is therefore evaporated, and the product, called blue salt, is mixed with half its weight of pure potassium carbonate for use in a subsequent melting operation.

Blue salt contains, besides potassium carbonate, potassium sulphide, sulphate, silicate, and chloride, as well as traces of other salts. Blue salt is often treated for the production of impure Prussian blue.

The insoluble residue remaining after the first lixiviation of the melted mass is washed once or twice with fresh quantities of water, and the liquor thus obtained is used for the lixiviation of fresh material. The residue remaining contains over 10 per cent. of potash, but it is thrown away as worthless, and thus considerable loss is occasioned. This loss of potash is less in proportion to the purity of the animal substances used.

Havrez recommends treating suint of sheep for both potassium carbonate and ferrocyanide. When suint of sheep is incinerated potassium carbonate is obtained, mixed with a considerable quantity of potassium cyanide, and on this account it would be suitable for the preparation of potassium ferrocyanide. The direct use of wool suint as nitrogenous material is also recommended by the above chemist.

Recrystallisation of the Crude Salt.—The crude salt is dissolved in hot water, or in the mother liquor of a previous crystallisation, and the solution cooled down very slowly, so as to secure the formation of large and clear crystals. For the same purpose pieces of string are often supported in the crystallising vessels, in order that crystals may adhere to them.

Uses.—Potassium ferrocyanide is chiefly used for the preparation of potassium cyanide, hydrocyanic acid, and Prussian blue; also in dyeing and calico-printing for producing blue colours. It is also useful as a reagent in analytical operations.

POTASSIUM FERRICYANIDE.

Formula $K_6Fe_2Cy_{12}$. Molecular Weight 658·6.

Composition.—This salt, also known as red prussiate, or as Gmelin's salt, etc., is the representative of a number of saline compounds, that may be regarded as containing a compound radicle $C_{12}N_{12}Fe_2$, which is sometimes represented by the symbol Cfdy.

Characters.—It forms beautiful transparent garnet red crystals, which belong to the monoclinic system. The salt is easily soluble in water, but scarcely at all soluble in alcohol.

Preparation.—Potassium ferricyanide is obtained by acting upon potassium

ferrocyanide with chlorine, the reaction consisting in the removal of one atom of potassium from the molecule of the salt:

$$2K_4FeCy_6 + 2Cl = K_6Fe_2Cy_{12} + 2KCl.$$

Potassium ferricyanide is prepared on a large scale by passing chlorine gas into a hot solution of potassium ferrocyanide having a specific gravity of 1·085, until a sample no longer gives a dark blue precipitate when tested with a solution of ferric salt, but only a clear brown liquid. When this point has been reached the liquid is evaporated in a copper vessel to a specific gravity of 1·216. The boiling hot liquor is then made slightly alkaline by the addition of a solution of potash filtered through linen, and left to crystallise in copper vessels. The potassium ferricyanide forms beautiful prismatic crystals, while the potassium chloride remains in the mother liquor, together with some potassium ferricyanide, which may be obtained in a less pure state by further evaporation.

A preparation known as blue powder is prepared by treating finely-powdered potassium ferrocyanide with chlorine. It consists of a mixture of potassium ferricyanide and potassium chloride. By treating the salt with water and crystallising once or twice it is easy to obtain from it pure potassium ferricyanide.

Reichardt suggests the use of bromine in the place of chlorine for preparing potassium ferricyanide. There is no doubt that the required change would be brought about as well by bromine as by chlorine, but probably bromine would prove too dear for the preparation of potassium ferricyanide on a large scale.

Uses.—Potassium ferricyanide is used in dyeing and calico-printing, for producing blue colours on wool and cotton fabrics. It is also useful as a reagent in analysis.

PRUSSIAN BLUE.

Under the name of Prussian blue are comprised three different kinds of blue pigment, all of which owe their colour to ferrous or ferric cyanide. The purest of them is Paris blue, consisting entirely of ferric ferrocyanide, $Fe_43(FeCy_6)$; after it comes Prussian blue, which is contaminated with alumina, starch, and similar substances; the third pigment, called mineral blue, is the most impure, being mixed with large quantities of chalk, heavy spar, clay, starch, etc., and it is of a lighter colour than the others.

Pure ferric ferrocyanide, or Paris blue, is prepared by mixing an aqueous solution of potassium ferrocyanide with an excess of a solution of ferric salt, such as ferric nitrate. The reaction which takes place is as follows:—

$$3K_4FeCy_6 + 2\left\{\begin{matrix}Fe_2\\6NO_3\end{matrix}\right\} = Fe_43FeCy_6 + 12\left\{\begin{matrix}NO_2\\K\end{matrix}\right\}O.$$

The precipitate formed is washed several times with water by a process of decantation, and then thrown upon a linen bag to drain off the moisture, and allowed to dry slowly. When it has attained a sufficient consistency for moulding it is either cut into squares or pressed into moulds, and the pieces are afterwards dried in the air.

Prussian blue is prepared by mixing an aqueous solution of potassium ferrocyanide with an excess of ferrous salt dissolved in water. A white precipitate is thus produced, which is converted into the dark ferric-ferrocyanide, or Prussian blue, by treating it with hydrochloric acid and calcium hypochlorite. The precipitate consists of potassio-ferrous ferrocyanide, $K_2Fe(FeCy_6)$, if the air is excluded, and there is no ferric salt present; it is formed according to the following equation:

$$K_4FeCy_6 + FeCl_2 = K_2Fe(FeCy_6) + 2KCl.$$

The precipitate rapidly turns blue by exposure to the air and by other oxidising agents, owing to the production of ferric ferrocyanide, as shown by the following equation:

Potassio-ferrous ferrocyanide			Prussian blue		Potassium ferrocyanide		Ferric oxide
$6K_2Fe(FeCy_6)$	+ 3O	=	$Fe_43(FeCy_6)$	+	$3K_4(FeCy_6)$	+	Fe_2O_3

The oxidised blue product is not entirely ferric ferrocyanide, for another reaction also takes place when the white precipitate is treated with oxidising agents, which is usually done in making Prussian blue, and as is shown by the following equation, part of the potassio-ferrous ferrocyanide is converted into potassio-ferrous ferricyanide:

$$2K_2Fe(FeCy_6) + O = 2KFe(FeCy_6) + K_2O.$$

Ordinary Prussian blue is, therefore, generally a mixture of ferric ferrocyanide

with potassio-ferrous ferricyanide, the proportions varying according to the method of manufacture.

In the preparation of ordinary Prussian blue very crude potassium ferrocyanide is chiefly used, which contains considerable quantities of potassium carbonate, and iron alum is often added for the purpose of neutralising it. In this way potassium sulphate and aluminum hydrate are formed, and the alumina remains mixed with the Prussian blue. When it is desired to retain the aluminum hydrate—which is generally the case—the oxidation must not be effected by the agency of calcium hypochlorite and hydrochloric acid, which would dissolve the aluminum hydrate, but the oxidation is in such case effected by exposing the mixture to the action of the air.

Mineral blue is produced by mixing Prussian blue with the above-mentioned foreign ingredients, the Prussian blue itself being for this purpose prepared from the most impure liquors of the potassium ferrocyanide manufacture.

Turnbull's Blue.—This pigment likewise consists of ferrous and ferric cyanides, but its constitution differs from that of Prussian blue. This may be seen from the following equation, which represents the formation of Turnbull's blue by the action of potassium ferricyanide upon a solution of a ferrous salt:

$$\underset{\text{ferricyanide}}{\text{Potassium}}\ K_6(Fe_2Cy_{12}) + \underset{\text{chloride}}{\text{Ferrous}}\ 3FeCl_2 = \underset{\text{ferricyanide}}{\text{Ferrous}}\ Fe_3(Fe_2Cy_{12}) + 6KCl.$$

Soluble Prussian blue is obtained most conveniently according to Brücke in the following way:—A solution of 1 part ferric chloride, in 10 parts water, is mixed with double its volume of a saturated solution of Glauber's salt, and the whole stirred up with an equal volume of a mixture consisting of a solution of potassium ferrocyanide (containing per litre 217 grams of the salt), with double its volume of a saturated solution of Glauber's salt. The precipitate formed is washed by decantation with distilled water, until the waste water becomes coloured. The residue is dried at the ordinary temperature and dissolves in water, forming a dark blue liquid.

Reindel prepares soluble Prussian blue by dissolving 1 part iron wire in aqua regia, and adding to the solution an aqueous solution containing 7·5 parts of potassium ferrocyanide and a small quantity of alcohol; the precipitate thus obtained is washed with a small quantity of water and dried in the air. The precipitate is rendered insoluble by heating it to 100°.

Use.—Prussian blue is chiefly used as a pigment in oil and water-colour painting, also in dyeing and calico-printing, the colour being produced within the fibres themselves, or printed upon the fabrics.

FUEL.

History.—The application of artificially produced heat for cooking food and for various domestic purposes appears to have been always a prominent feature of distinction between mankind and the lower animals; but until a comparatively recent date, the use of combustible materials as a source of heat (fuel) was for the most part restricted to the warming of dwellings and the preparation of food, and, beyond the forging of iron and the smelting of other metals, its industrial applications seem to have been but few. In later times, however, as the industrial arts developed, the artificial production of heat by the use of fuel became one of the most important means of effecting the chemical changes that take place in manufacturing operations; and since the invention of the steam engine furnished the means of converting heat into motive power, the use of fuel as a source of heat has become so extensive in connection with industrial art and commercial intercourse, that there is scarcely any branch of industry or trade that is not to some extent dependent upon it, either directly or indirectly.

Up to the thirteenth century, wood was probably the chief, if not the only, material used to any great extent as fuel, and the burning of coal for any purpose in the city of London was for a long time rigorously prohibited by law. Even so late as the year 1779, the quantity of coal imported into London was only about 800,000 tons. But in the fifteenth century, the consumption of wood in the smelting of iron had become so considerable, and the consequent destruction of timber so serious, that Acts of Parliament were passed to restrict its use for that purpose. Shortly afterwards coal was successfully substituted for wood in iron smelting, and since the middle of the eighteenth century it has been the chief fuel used in the manufacture of iron, as well as in most other industrial operations.

Composition and Characters.—The various materials used as fuel are all,

either directly or indirectly, of vegetable origin, and they consist either of the unaltered ligneous tissue of plants, as in the case of wood and some varieties of turf and peat, or of products resulting from the alteration of vegetable materials by decay, as in the case of the various kinds of peat, lignite, coal, etc. In all kinds of fuel consequently there is a general similarity of elementary composition, accompanied, however, by considerable difference in the relative proportions of the elementary constituents, and by specific differences of character, depending sometimes more upon the physical structure and constitution of particular kinds of wood, peat and coal, or the mode in which their elementary constituents are chemically arranged, than upon their actual amounts.

In all cases, the chief elementary constituents of the materials used as fuel are carbon and hydrogen, combined with some oxygen, and a very small proportion of nitrogen. Besides these constituents, which together make up the principal mass of all kinds of fuel materials, and constitute the organic combustible portion, there is always some proportion of incombustible earthy or inorganic substance that remains as ash when the fuel is burnt, and originates either entirely from plant tissues, as in the case of wood, or partly also from mechanical admixture of earthy substances, such as mud, sand, etc., with the carbonaceous materials from which a particular kind of fuel has been formed, as in the case of coal. Some of the materials used as fuel also contain, in the raw state, a considerable amount of water, according to the porous or compact texture of the material and its hygroscopic character; this is especially the case with wood, peat, and lignite, but the amount of water in coal is seldom considerable.

The amount of ash in different kinds of fuel varies considerably. In wood it is seldom much more than 1 per cent.; but in some kinds of lignite and coal it rises as high as 10 or even 20 per cent.; as a general average, 5 per cent. is as much as there should be in fuel of good quality.

The water actually existing in fresh wood and in air-dried turf and peat may amount to upwards of 40 per cent. and even in ordinary air-dried wood as well as in peat and lignite it is seldom less than 20 per cent.; in coal the amount of water is always very much less.

The following tables give the average composition of different kinds of fuel.

	Cellulose or Lignin	Wood		Turf	Peat		Lignite
		air-dried	dried at 140°	air-dried	air-dried	kiln-dried	air-dried
Carbon .	44·44	40·36	50·45	35·3	46·1	60·0	49·24
Hydrogen .	6·17	4·91	6·14	3·6	4·6	6·9	4·18
Oxygen .	49·39	32·66	40·83	19·2	23·6	30·0	16·97
Nitrogen .	—	·90	1·11	·7	1·0	1·2	0·41
Sulphur .	—	—	—	—	—	—	1·75
Ash . .	—	1·17	1·47	1·1	1·5	1·9	1·69
Water . .	—	20·00	—	40·1	23·2	—	25·75
	100	100	100	100	100	100	99·99

Wood.—There is but little difference in wood as regards its composition, which approximates closely to that of pure woody fibre, and its applicability as fuel depends chiefly upon its density and structural peculiarities, according to which, the different kinds of wood are distinguished as hard, like oak, beech, elm, alder, etc., or soft, like pine, fir, willow, and poplar woods. The weight of a cubic foot of wood varies from 26 to 42 lbs.

Turf and Peat consist of the remains of mosses and other plants that have undergone some degree of alteration. In many cases, the plant structure remains almost perfect, and the material has a spongy fibrous character. Sometimes, however, the entire mass has been converted into a pasty condition like clay, with only slight indications of the organised structure, and the term peat should be restricted to these varieties. In consequence of this difference of texture, the density of turf and peat varies from 0·2 to 1·23, and the weight of a cubic foot from 12 pounds to 78 pounds.

Both peat and turf, as they usually occur in bogs or on the side of mountains, contain from 80 to 90 per cent. of water, and in the ordinary air-dried condition they contain from 20 to 40 per cent.

As regards composition, there is but little difference between the various kinds of turf and peat, and their applicability as fuel depends chiefly upon their physical character. They are generally somewhat more carbonaceous than wood.

Lignite or brown coal consists of plant remains still retaining their struc-

ture in a distinctly recognisable condition, though they have undergone alteration to greater extent than turf or peat. The density of lignite is generally much greater than that of peat, varying from 1·1 to 1·85, and the cubic foot weighs on the average about 80 pounds.

In composition, lignite approximates to wood, but it is more highly carbonaceous in proportion to the degree of alteration it has undergone. .

Coal.—Under this name are comprised the different kinds of mineral carbon and a great variety of highly carbonaceous combustible minerals that are capable of being used as fuel, and indeed are by far the most important materials applied to this purpose. Coal has probably in all cases originated, like other combustible carbonaceous minerals, from the gradual alteration of vast masses of the remains of plants which flourished in great luxuriance at very remote periods of earth's history. The general chemical features of this alteration, by which the ligneous tissues of plants have been gradually converted into coal, consist in the elimination of water as well as oxygen and hydrogen, existing as constituents of the original plant remains, and the consequent proportionate increase of the amount of carbon in the residual mass. But differences in the particular nature of the original materials from which coal has been thus formed, as well as in the conditions under which the alteration took place and the extent to which it has advanced, have frequently influenced very considerably the character of the product, and consequently there are numerous varieties of coal presenting differences in their composition and characters that are sometimes very marked, though in general they are more differences of degree than otherwise.

The several kinds of coal may be conveniently classified under the two heads of Anthracite and Bituminous Coal; but this classification is entirely conventional, and is based only upon the presence or absence of certain characteristics affecting the practical application of coal as fuel.

A similar conventionality and vagueness attaches to the general definition of coal as a fuel material, and its distinction even in this respect alone from other analogous minerals, such as the carbonaceous shales, etc., that are frequently associated with coal, and have probably been formed from similar materials and in the same manner as coal, but are distinguished chiefly by containing large amounts of incombustible earthy admixture. From a practical point of view, any carbonaceous mineral that will burn may in a general way be regarded as coal; but, in some respects, its applicability as fuel may be greatly influenced by the amount of earthy substance it contains, and this often constitutes a good criterion as to whether a particular mineral should be regarded as coal or not.

	Anthracite	Merthyr	Duffryn	Hartley	Oldcastle	Hartley	Wigan
Carbon .	91·44	90·27	88·26	81·18	87·68	80·26	80·07
Hydrogen .	3·46	4·12	4·66	5·56	4·89	5·28	5·53
Oxygen .	2·58	2·53	0·60	8·03	3·39	2·40	8·10
Nitrogen .	0·21	0·63	1·45	·72	1·31	1·16	2·12
Sulphur .	0·79	1·20	1·77	1·44	·09	1·78	1·50
Ash . .	1·52	2·53	3·26	3·07	2·64	9·12	2·70
	100	101·28	100	100	100	100	100·02

Anthracite is characterised by containing a larger amount of carbon than any other kind of coal. It is very dense, hard, and brittle. It is less readily combustible than almost any other kind of fuel, and it requires a strong draught or blast for its combustion. When suddenly heated, anthracite decrepitates and crumbles into small fragments, a character which makes anthracite difficult to burn without considerable waste.

The various kinds of bituminous coal are generally less carbonaceous than anthracite, and they contain relatively larger proportions of hydrogen and oxygen. There is not, however, any recognisable relation between their specific characters and their elementary composition. Bituminous coal is generally characterised by containing a considerable amount of bituminous substance which is decomposed by heat, yielding volatile tarry and gaseous products, and consequently burns with flame. In this respect it differs widely from anthracite, which contains little volatilisable substance and burns without flame. Some bituminous coal undergoes a kind of imperfect fusion when heated, softening and swelling up considerably from the evolution of gas while decomposing, and ultimately forming a bulky porous mass of carbon. Coal of this kind is termed caking coal. Other kinds of bituminous coal which retain their solidity

and form when heated, but split into columnar fragments when burnt, are commonly termed dry or free-burning coals. Another kind of bituminous coal, containing a large amount of bituminous substance volatilisable by heat, is termed cannel coal. The specific gravity of bituminous coal varies from 1·2 to 1·5, the cubic foot weighing from 70 to 90 pounds.

Since the value of any material as fuel is proportionate to the combustible substance it contains, the presence of any considerable amount of earthy substance or of water is objectionable on that account alone. The presence of earthy substances has likewise the disadvantage of causing inconvenience when the fuel is burnt, by the melting or caking of the earthy residuum and the formation of slag or clinker upon the fire bars of the furnace. The presence of water in fuel is also attended with a further disadvantage, consisting in the consumption of heat for the vaporisation of this water, so that some portion of the heat actually produced by burning the fuel is thus expended uselessly and with a proportionately inferior practical effect.

When any material containing water is used as fuel, the quantity requisite for producing a given effect is therefore proportionally greater than it would be if the fuel were free from water. For some purposes, such as evaporation or heating liquids, no great advantage would be gained by drying the fuel artificially before burning it, since the consumption of heat in drying would be equal to the waste attending the use of the fuel in its raw state. The case is different, however, when fuel is used with the special object of producing a high temperature, for the temperature attainable by the combustion of a material is absolutely limited by the presence of water in any considerable amount, and it is only by previously drying the fuel that it is possible to produce a high temperature. It is on this account that wood and similar materials are subjected to the operation of kiln drying to render them more suitable for use as fuel, when high temperature is one of the effects they are intended to produce.

The amount of heat that any material is capable of producing when used as fuel, depends principally upon the composition of the combustible portion, and to some extent also upon special peculiarities of its constitution, structure, and condition, by which its combustion is influenced. Carbon and hydrogen, the heat-producing constituents of all kinds of fuel, differ considerably in regard to the amount of heat they produce when burnt. Carbon burnt to carbonic dioxide evolves heat sufficient to raise the temperature of 8,000 times its weight of water one degree, and hydrogen when burnt evolves heat sufficient to raise the temperature of 3,3881 times its weight of water one degree, or 4·23 times as much as an equal weight of carbon. For the purpose of expressing the relative heat-producing power of fuel, carbon is taken as the standard of comparison, and the heat it evolves when burnt to carbonic dioxide as the unit of calorific power.

When the combustible portion of fuel consists entirely of carbon, as in the case of charcoal or coke, its relative calorific power p corresponds with the amount of carbon C, in the fuel.

When the combustible portion of fuel contains hydrogen as well as carbon, the calorific power referrible to this constituent is found by multiplying its percentage amount by 4·23, and adding the product to the number expressing the amount of carbon; thus $p = C + 4{\cdot}23\ H$.

When fuel contains oxygen, this constituent must be regarded as being already in combination with an equivalent quantity of hydrogen, and when the fuel is burnt a corresponding quantity of water is produced in addition to that actually existing in the material. Thus, for instance, kiln-dried wood containing about 41 per cent. of oxygen and 6 per cent. of hydrogen will produce in burning more than half its weight of water, the greater part of which is formed by the combination of some of the hydrogen with the oxygen that constitutes part of the wood. This combination of hydrogen with oxygen existing in the wood is not attended with evolution of heat, and only the carbon and the surplus hydrogen over and above the quantity equivalent to the oxygen present in the fuel evolve heat in the combustion of a material containing oxygen. Practically, therefore, the heat-producing capability of such a material as wood, even when kiln dried, is limited by the amount of oxygen it contains. In other words, when materials containing oxygen are burnt as fuel, only those portions of the carbon and hydrogen are capable of evolving heat which can be regarded as though existing in the free state. As a result of this important fact, the efficiency of wood or any other material containing a considerable amount of oxygen is very much less than that of materials containing no oxygen. In the case of kiln-dried wood only the carbon, and about one-sixth part of the hydrogen it contains, generate heat when the wood is burnt. Therefore, in expressing the relative calorific power of a material containing oxygen, a deduction must be made from the total amount of hydrogen equal to one-eighth of the oxygen present, and in such cases $p = C + 4{\cdot}23\ (H - \frac{1}{8}O)$.

In all kinds of fuel containing hydrogen and oxygen, the hydrogen is in excess of

the quantity requisite for forming water with the oxygen. This is the case even with wood, although the cellulose of which it chiefly consists has the composition of a carbohydrate. This excess of hydrogen in wood is due to the presence of resin and similar substances. In other kinds of fuel, such as peat, lignite, and coal, the excess of hydrogen over and above that requisite to form water with the oxygen they contain is still greater. The excess of hydrogen in these cases appears to indicate that in the alteration of plant remains, by which these materials have been formed, oxygen has been to a great extent eliminated in combination with carbon and not altogether as water. A similar result may sometimes be produced in the combustion of fuel, and in that case, according to the amount of hydrogen capable of being burnt, a proportionately greater amount of heat would be produced, since the calorific power of hydrogen is 4·23 times that of carbon. In such cases $p = C - \frac{3}{8}O + 4{\cdot}23\ H$.

The calorific power of fuel may be expressed in heat-units by multiplying the amount of carbon and the amount of available hydrogen in one part of the fuel respectively by the numbers expressing in heat units the calorific power of carbon and of hydrogen; the sum of these two products represents the calorific power of the fuel in heat-units:

Fuel containing only carbon . .	$p = 8000\ C$
Fuel containing carbon and hydrogen	$p = 8000\ C + 33881\ H$
Fuel containing carbon, hydrogen, and oxygen . . .	$p = 8000\ C + 33881\ (H - \frac{1}{8}O)$.

The numerical expression of calorific power in heat units will of course be different according as the thermometric scale to which it refers is that of Celsius, Fahrenheit, or Réaumur, since the degrees of these scales are in the ratio of 1 : 1·8 : 0·8. The value of the heat unit as a definite quantity will also be different according to the unit or weight as well as the thermometric scale referred to. According to the centigrade scale and the metrical system of weights, the heat unit is the quantity of heat which raises the temperature of one kilogram of water from 4° to 8°C, while the heat unit, according to the Fahrenheit scale and the British system of weights, is the quantity of heat which raises the temperature of a pound of water from 40° to 41° F. Consequently these two values bear the following ratio to each other:

British heat unit		French heat unit
1	=	0·251996
3·96832	=	1·

In the following table the calorific power of several combustible materials is given both relatively and in heat-units of the centigrade as well as the Fahrenheit scales.

The figures in column 2 represent the average in decimal parts of the respective proportions of the elementary constituents, ash, etc., in one part of the different materials. Column 3 gives the weight of oxygen requisite for converting the combustible carbon and hydrogen in one part of each material into carbon dioxide and water.

The numbers in column 7 of the accompanying table are obtained by dividing those in column 5 by 100 or those in column 6 by 180, upon the assumption that equal quantities of heat are requisite for raising the temperature of x parts of water y degrees or y parts of water x degrees. Thus the heat evolved by the combustion of one pound of carbon would be sufficient to raise the temperature of 8000 pounds of water from 4° to 5° or of 80 pounds of water from 0° to 100°. This assumption, however, is not strictly correct, since the specific heat of water increases slightly as the temperature exceeds 4°, the point of its maximum density; but the data in the table are sufficiently exact for ordinary purposes.

The numbers in column 8 are obtained by dividing those in column 7 by 5·37, on the assumption that the quantity of heat requisite to convert water at the boiling point into steam under the normal atmospheric pressure, is 5·37 times as much as is requisite for raising the temperature of the same weight of water from 0° to 100°.

A comparison of the data given in this table will show clearly the influence exercised by the presence of oxygen in the materials used as fuel, not only by reducing the actual amount of carbon and hydrogen, but also by rendering some portion of one or both of those substances useless for the production of heat, inasmuch as they are already combined with the oxygen. This is very evident in the case of carbonic oxide, which gives 1731 heat units by combustion, or only half as much heat as would be produced by the combustion of a quantity of carbon equal to that contained in the unit of weight of carbonic oxide. In fact, so far as regards the production of heat corresponding to the oxidation of carbon to carbon dioxide, one-half of the carbon in carbonic oxide may be regarded as if it were already in the state of carbon dioxide, since the heat evolved by the combustion of carbonic oxide is only half that evolved by the combustion of a quantity of carbon equal to the carbon contained in that gas.

1	Composition of Fuel					3	4	5	6	7	8
	Carbon	Hydrogen	Oxygen	Ash	Water	Oxygen requisite for combustion	Calorific power: Relative	heat-units: Centigrade	heat-units: Fahr.	Water heated from 0° to 100°	Water at 100° converted into steam
HYDROGEN .	—	1·	—	—	—	8·	4·23	33881	60986	338·81	63·
MARSH GAS	0·75	0·25	—	—	—	4·	1·81	14470	26046	144·7	26·9
OLEFIANT GAS	0·857	0·143	—	—	—	3·43	1·46	11701	21062	117·0	21·8
COAL:											
Welsh .	0·838	0·048	0·041	0·049	—	2·58	1·02	8161	14690	81·6	15·2
Newcastle .	0·821	0·053	0·057	0·038	—	2·56	1·01	8126	14627	81·2	15·1
Carbon .	**1·**	—	—	—	—	**2·67**	**1·**	**8000**	**14400**	**80·0**	**14·9**
COAL:											
Scotch .	0·785	0·056	0·097	0·040	—	2·53	0·97	7771	13988	77·7	14·5
Derbyshire .	0·797	0·049	0·101	0·026	—	2·42	0·95	7596	13673	75·9	14·1
Lancashire	0·779	0·053	0·095	0·049	—	2·41	0·95	7621	13718	76·2	14·2
PEAT:											
Kiln-dried .	0·60	0·060	0·307	0·020	—	1·78	0·69	5545	9981	55·4	10·3
Air-dried .	0·461	0·046	0·246	0·015	0·232	1·23	0·52	4196	7553	41·9	7·8
WOOD:											
Dried at 140°	0·503	0·061	0·407	—	—	1·42	0·54	4363	7853	43·6	8·1
Air-dried	0·404	0·049	0·327	—	0·200	1·14	0·44	3503	6305	35·0	6·5
CARBONIC OXIDE .	0·43	—	0·57	—	—	0·57	0·21	1731	3116	17·3	3·1

The practical effect produced by any material used as fuel is always less than its calorific power would indicate, and the amount of this difference depends upon a number of conditions, among which the elementary composition is one of the most important in its influence. To illustrate the nature of this difference between the calorific power of fuel and its practical efficiency, it will be necessary to consider how the heat actually evolved in burning fuel is disposed of. In any case of the combustion of fuel, the total heat evolved is communicated to the product of combustion, which is in all ordinary cases gaseous, producing in it at the moment of combustion a temperature determined partly by the calorific power of the fuel, and partly by the nature as well as the amount of the product of combustion. Thus, for instance, taking the simplest case, carbon requires for its combustion to carbonic dioxide 2·67 times its weight of oxygen, and by combining with oxygen, it produces 3·67 times its weight of carbonic dioxide. Since atmospheric air is the source of the oxygen that supports the combustion, and since it contains only 23 per cent. of oxygen by weight, the quantity of air containing the 2·67 parts of oxygen requisite for the combustion of the carbon will be 11·61 times the weight of the carbon burnt, and the 3·67 parts of carbonic dioxide produced will be mixed with the 8·94 parts of nitrogen contained in that quantity of air, making the gaseous product of combustion in all 12·61 times the weight of the carbon burnt.

The heat evolved by the combustion and distributed throughout the quantity of mixed gas is 8000 heat units, and it is sufficient to raise the temperature of a quantity of water 8000 times the weight of the carbon burnt one degree, or of a quantity of water equal to the weight of mixed gas resulting from the combustion 635 degrees.

$$8000 \times 1° = 12{\cdot}61 \times 635°.$$

But since the specific heat of carbonic dioxide, as well as that of nitrogen, or the quantities of heat requisite to raise the temperature of these gases one degree, is much less than the specific heat of water, the increase of temperature of the mixed gas resulting from the combustion is proportionately greater than 635°.

The specific heat of carbon dioxide is only 0·2164 as compared with that of water = 1·, and the specific heat of nitrogen is 0·244: hence the quantity of heat requisite to raise the temperature of the mixed gas produced by the combustion of the unit of weight of carbon will be as follows:

Products of combustion	Weight relatively to carbon burnt	Specific heat	Heat-units	
Carbon dioxide . .	3·67 ×	·2164 =	0·794	= 2·975 heat-units;
Nitrogen	8·94 ×	·244 =	2·181	

and the 8000 heat-units will therefore raise the temperature of the mixed gas:

$$2689° = \frac{8000}{2{\cdot}975}.$$

Under ordinary circumstances, however, the effect produced by burning fuel is considerably less than that indicated by the above calculation; for by the combination of oxygen with carbon and hydrogen there is a constant tendency to the production of an atmosphere of carbonic dioxide, water vapour, and nitrogen in the furnace; and in order to maintain a sufficiently rapid combustion, it is necessary to remove these products of combustion and to supply air in greater proportion than is necessary for the mere oxidation of the carbon and hydrogen, so as to sweep the products of combustion out of the furnace, and keep the fuel surrounded with an excess of oxygen. Practically the quantity of air requisite for this purpose, when fuel is burnt with a chimney-draught, amounts to about twice as much as is necessary for converting the combustible constituents of fuel into carbon dioxide and water-vapour.

In this way the product of combustion throughout which the heat is distributed is doubled in quantity, and there is in consequence a proportionate reduction in the temperature produced. The specific heat of atmospheric air is 0·2377, and the quantity requisite for raising the temperature of 11·61 pounds of air one degree will therefore be $2·7596 = 11·61 \times ·2377$; and this quantity, added to the 2·975 in the above calculation, gives 5·7346 heat-units as the quantity of heat requisite for raising the temperature of the total mixed gas one degree, and therefore the 8000 heat-units will produce an increase of temperature of only $1,394° = \frac{8000}{5·7346}$, or half as much as the result previously calculated, because the quantity of gas to be heated is twice as great.

It will therefore be evident that the admission into a furnace of more air than is actually requisite will be attended with proportionate waste of heat; and so far at least as the production of a high temperature is concerned, it is always desirable to effect combustion with the smallest possible amount of air. If air be forced into a furnace by means of a fan or other kind of blowing apparatus, as in a forge, fuel may be burnt rapidly with much less air than when combustion is supported by a chimney-draught.

The amount of heat evolved in the combustion of hydrogen is much greater than that evolved in the combustion of carbon, but the effect produced as regards increase of temperature is not much greater than in the combustion of carbon, for hydrogen requires for combustion three times as much oxygen as carbon does, and therefore the mixed gas resulting from its combustion amounts to three times as much as in the case of carbon. In the formation of water vapour by the combustion of hydrogen, heat is rendered latent and ineffective for increasing the temperature of the gaseous product. The latent heat of water, or the quantity of heat requisite to convert the unit of weight of water at 100° into steam, is 537 times as much as is requisite to raise the temperature of an equal weight of water one degree. Therefore the quantity of heat that becomes latent in the nine parts of water vapour produced in the combustion of hydrogen will be 4833 heat-units = 9 × 537, and this must be deducted from the total heat evolved in order to ascertain the quantity available for producing increase of temperature. Moreover, the specific heat of water vapour—the product of combustion—is more than double that of carbon dioxide. Consequently the heat evolved in the combustion of hydrogen, amounting to 33,881 heat-units for the unit of weight, is not only distributed through a greater quantity of mixed gas, but part of it becomes latent by the formation of water vapour, and a greater proportion of the remainder is required to raise the temperature of the gas.

The specific heat of water vapour is 0·475 as compared with that of water in the liquid state, and the quantity of heat requisite to raise the temperature of the mixed gas resulting from the combustion of hydrogen will be as follows:—

Products of combustion	Weight relatively to hydrogen burnt		Specific heat		Heat-units	
Water vapour . . .	9·	×	0·475	=	4·2750	= 19·076.
Nitrogen	26·78	×	0·244	=	6·5340	
Surplus air . . .	34·78	×	0·2377	=	8·2672	

Consequently the available heat, amounting to 29,048 heat-units = 33881 − 4833, will raise the temperature of the mixed gas only $1,522° = \frac{29048}{19·076}$.

This comparison of the effects produced by carbon and hydrogen serves to illustrate the influence exercised by the presence of water vapour in the products of combustion upon the efficacy of fuel, so far as regards the production of high temperature. When the water vapour is formed either from water actually existing in materials used as fuel or from hydrogen and oxygen that do not evolve heat by their combination, as is the case when wood or materials of similar composition are burnt as fuel, its presence

is especially disadvantageous, since its influence in reducing the temperature of combustion is not compensated for by the large amount of heat evolved in the combustion of hydrogen.

It is for this reason that the practice of charring or carbonisation has been adopted whenever materials such as wood have to be used as fuel for producing high temperatures. In charring any kind of fuel the whole of the water that it actually contains is separated, as well as that corresponding to, and capable of being produced by, the oxygen in the material. At the same time some of the carbon is volatilised partly in the state of carbonic oxide and dioxide, partly also in the state of hydrocarbon compounds. But though carbonisation always involves absolute loss of some portion of heat-producing material, and though in the case of wood it furnishes, in the form of charcoal, little more than one-half of the carbon existing in the wood. the practice is advantageous on account of the greater efficacy of the carbonaceous product obtained.

The same principle holds good in regard to other materials besides wood, though the advantage gained, so far as removal of water is concerned, is in this case only proportionate to the amount of oxygen in the materials. There are, however, other effects produced by the carbonisation of some materials which are equally, if not more, beneficial as regards their applicability as fuel.

In burning certain kinds of raw coal and other materials, a considerable portion of the carbon they contain is volatilised in the form of hydrocarbon compounds. Such materials burn with flame, and for some purposes, such as the heating of steam boilers, this character is to a certain extent advantageous. But when the amount of volatilisable substance is large, it gives rise to such copious evolution of highly carburetted gas and vapour that complete combustion of the fuel is scarcely possible. In many cases where fuel has to be burnt rapidly, as in steam-boiler furnaces, the hot carbonaceous gases are swept away towards the chimney before being burnt, and as their temperature is reduced by contact with the boiler flues, the unoxidised carbon they contain is deposited in the form of soot and smoke. The tendency to the production of soot and smoke in this way is proportionate to the amount of volatilisable carbonaceous substance in the material burnt, and to the amount of carbon in the vapour produced. Besides the waste of heating power resulting from the production of soot and smoke, there are manifold other inconveniences attending the use of such materials as fuel, and for these reasons it is often more advantageous to carbonise them than to use them in the raw state. Moreover, caking coal, which undergoes a kind of imperfect fusion when heated, and becomes pasty while decomposing, is on this account unsuitable for some metallurgical operations until, by the process of carbonisation, it is converted into hard coke that will burn without softening or volatilising, and be more capable of supporting the superincumbent weight of large masses of heavy material.

The extent to which volatilisation of carbonaceous substance takes place in carbonising different materials depends very much upon their nature, and likewise upon the mode in which the operation is conducted. As a rule the amount of carbonaceous residue obtainable from any given material is greatest when the carbonisation is conducted slowly. In the case of wood the difference between the result of rapid and slow carbonisation may amount to as much as 9 or 10 per cent. of the wood carbonised. In carbonising coal the difference is not so great, and in a general way the amount of coke obtainable depends more upon the particular character of the coal.

In the foregoing considerations it has been assumed that in the use of any material as fuel the whole of its combustible constituents are completely converted into carbonic acid and water vapour, and the calculated effects express the highest capabilities of fuel as compared with pure carbon and when burnt under the most favourable conditions.

SULPHUR.

Symbol S. Atomic Weight 32.

History.—This substance has been known from the earliest times under the name of brimstone (from *Brennestein*, the burning stone). Its elementary nature was not recognised until the time of Lavoisier.

Occurrence.—Sulphur is found abundantly in the free state, and in chemical combination with other substances it occurs in still larger quantities.

In the free state sulphur is chiefly found in volcanic districts, where, amongst other modes of formation, it is often produced by the action of sulphurous oxide upon sulphuretted hydrogen, both of which substances occur in volcanic exhalations. The decomposition takes place according to the equation:

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

Sulphur is also eliminated when sulphuretted hydrogen gas comes into contact with water vapour and a small quantity of air at a high temperature; it is also set free by the decomposition of the higher metallic sulphides, which give up a portion of their sulphur when heated. The sulphur thus given off in the state of vapour condenses in the form of a moist mud, and gives rise to beds of sulphur, such as those occurring in Sicily, Poland, etc. Sulphur is also produced by the reduction that sulphates (especially gypsum) undergo in contact with decaying vegetable remains. The largest deposits of native sulphur occur in Sicily, where entire beds of rock, generally limestone or blue clay, are found highly impregnated with it. Sulphur is also found in the native state at Urbino Reggio in Italy, in Croatia, near Lüneburg in Poland, on the shores of the Red Sea, and in smaller quantities in many other places. It occurs likewise, in the volcanic exhalations of Vesuvius and Etna, also in Iceland, in the Lipari Isles, and in the Solfatara of Naples and Tuscany.

Sulphur exists in various states of chemical combination with a very large number of metals: iron pyrites, copper pyrites, galena, and blende being the most frequent among the compounds of sulphur with metals. It exists also in the form of sulphates, of which the most abundant are gypsum, Epsom salts, heavy spar, and copperas. Free sulphuric acid has been detected among the products of volcanic activity. Mineral water frequently contains sulphur as sulphuretted hydrogen and as sulphides.

Lastly, sulphur exists very extensively in the organised products of the vegetable and animal kingdom, being found in the ethereal oils of mustard, horse-radish, onions, etc.; also in albumen, gluten, and casein, as well as in hair and wool, etc.

Characters.—At the ordinary temperature sulphur is solid, and of a pale yellow colour. At a temperature of 50° it becomes almost colourless. When rubbed, it emits a peculiar odour; it is brittle, a bad conductor of electricity and of heat, and has a specific gravity of 2·050.

Sulphur melts at 114·5°, exhibiting very peculiar phenomena when heated above that temperature, passing gradually from the condition of a pale yellow liquid into a viscous and dark coloured state, until at 250°–260° it becomes quite thick and almost black. Heated still further, it again becomes liquid, beginning to boil at a temperature of 420°, and being converted into a reddish brown vapour, the specific gravity of which relatively to air is 6·617 and its density as compared with hydrogen 96: it is only at a temperature of 1000° that sulphur vapour acquires its normal density of 32 as compared with hydrogen.

If sulphur heated to 350° or 400° be suddenly cooled by pouring it in a thin stream into cold water, it forms a soft brownish mass, which may be kneaded like dough, and has in this condition a specific gravity of only 1·957; after a time it passes again into the ordinary pale yellow brittle state. When a mass of melted sulphur is allowed to cool, it crystallises in long prismatic needles, which after a time are converted into octahedra, the ordinary form in which sulphur crystallises. When melted sulphur is cooled quickly, it forms a crystalline mass called roll sulphur. When sulphur vapour is rapidly condensed in chambers containing cold air, it forms a finely divided yellow crystalline powder, and in this state is called flowers of sulphur.

Milk of sulphur consists of sulphur in an extremely fine state of division, as it is precipitated from a solution of alkaline sulphides by means of acids.

Sulphur is insoluble in water, and sparingly soluble in alcohol, ether, or solution of ammonia; it is more easily dissolved by fat oils and by oil of turpentine. The best solvents for sulphur are carbon disulphide, chloride of sulphur, and ethyl sulphide. The solubility of sulphur in various solvents is shown in the following table:—

100 parts	Dissolve the following parts by weight of sulphur	
	At 100°	At 16°
Of carbon disulphide . . .	73·46	38·70
„ light coal oil	26·98	1·51
„ benzol	17·04	1·79
„ oil of turpentine . . .	16·16	1·30
„ petroleum	10·56	2·77
„ carbolic acid . . .	5·47	0·66 (at 35°)
„ ether	0·54	0·18
„ absolute alcohol . . .	0·42	0·12

Sulphur burns in the air with a blue flame. The product of combustion is sulphurous oxide, to which the unpleasant smell of burning sulphur is due. The process is one of simple oxidation, the sulphur combining with its own weight of oxygen:

$$\begin{array}{ccccc} S & + & 2O & = & SO_2 \\ 32 & & 32 & & 64 \end{array}$$

By combustion, sulphur yields 2221 units of heat, or less than an equal quantity of charcoal or coal. It is oxidised slowly when heated with nitric acid, and more rapidly when melted with nitrates.

In its chemical relations sulphur closely resembles oxygen, and many of the compounds of sulphur correspond with those of oxygen. Sulphur, like oxygen, is bivalent. It combines directly with hydrogen, chlorine, carbon, and some other elementary substances under the influence of a high temperature. Sulphur is also dissolved when heated with solutions of basic hydrates, with formation of sulphides.

Sulphur combines with most metals in several proportions; but combination takes place only at a high temperature. In the state of vapour sulphur combines with many metals with considerable evolution of heat and light.

Preparation.—Sulphur as it occurs naturally is always mixed with earthy material, stones, etc., and is separated from them by melting. Sulphur is also obtained from pyrites, a mineral consisting chiefly of iron disulphide, which is decomposed by heat with separation of one-third of its sulphur.

$$3FeS_2 = Fe_3S_4 + 2S.$$

Sulphur is also obtained as a by-product in roasting copper ores, and a considerable quantity is extracted from the 'soda waste' obtained in the manufacture of soda, as well as from the ferric hydrate used for purifying coal gas.

Extraction of Native Sulphur.—Native sulphur is obtained at a number of places in Sicily; but there are only about fifty places where the works are at all extensive. The most important sources are situated in the provinces of Caltanizetta, Girgenti, Catania, and Palermo. Bad roads, want of capital, imperfect methods of extracting and working the ores, have so far prevented the utilisation of these abundant deposits of sulphur, that it is often found more profitable to use pyrites as a source of sulphur.

The sulphur deposits in Sicily are worked very imperfectly. Steam-power is seldom employed for hauling up the excavated material, which is in most cases carried up from the mines in baskets by boys. The depth of the mines is inconsiderable; generally about 60 feet, and seldom as much as 100 feet.

On the shores of the Red Sea, in the neighbourhood of Suez, there are two beds or deposits of sulphur of comparatively pure quality, viz., Djemah and Ranga. At the first-mentioned place, a large mass of sulphur rises above the sand in the form of a hill 600 feet in height. This deposit has of late been worked by blasting, as in an ordinary stone quarry. The sulphur found at Ranga does not lie so near the surface as is the case at Djemah; it is, however, lighter coloured and purer.

Extraction of raw Sulphur in Kilns (calcarelle).—Fig. 28 represents a kiln, called calcarelle, which was universally in use up to 1851. It has the shape of an ordinary lime kiln, and is charged in the same way. Large lumps of earthy sulphur ore are

built up in the form of an arch at the bottom of the kiln, and the space above this arch is filled in with pieces continually decreasing in size, the top being covered with fine ore dust, and lastly with straw. Either the straw is set on fire, or the sulphur is ignited below, and a portion of it burns in either case; but the greater part is melted by the heat, and trickles down into the lower part of the kiln, flowing out from the opening (*g*) into a vessel (*h*) beneath, in which it solidifies. As it is necessary that a part of the sulphur should be burnt, in order to heat the whole mass, the kiln is furnished with lateral openings (*fff*), for admitting the necessary supply of air.

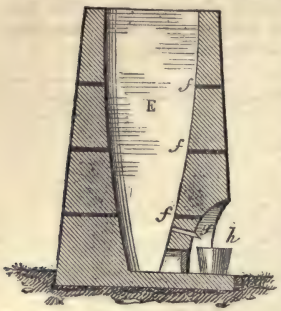


FIG. 28.

Kilns of this kind hold about 4 tons of ore; they yield only from 8 to 10 per cent. of sulphur from ore containing 30 per cent., or about one-third of the sulphur contained in the ore.

This method of refining sulphur has the disadvantage that a great deal of sulphur is lost, and large quantities of sulphurous acid are produced, which act very injuriously upon the surrounding vegetation.

Extraction in Stacks (*calcaroni*).—This method of extracting sulphur has an advantage over that just described, because less sulphurous acid is produced, and consequently less sulphur is lost. The sulphur ore is built up in stacks on a sloping hearth, and in the interior of the heap vertical spaces are left, open above, and capable of being covered with slabs of stone. Bundles of hay, which have been dipped in melted sulphur, are thrown into these openings, and set fire to, for the purpose of firing the entire heap. Twelve hours after the introduction of the burning bundles, the openings are closed with the stone slabs, and the whole heap or stack is covered with a layer of clay, earth, etc. At the lowest part of the sloping hearth of the stack there is a tap-hole, which is closed with a clay plug, so that all the melted sulphur flowing down from the sloping hearth collects at that point. This tap-hole is opened at intervals, and the sulphur run off into suitable vessels.

Small stacks are sometimes made containing from 3500 to 5000 cubic feet, but larger ones measuring 30,000 to 35,000 cubic feet are preferable. A stack of the latter size burns about two months.

By means of the apparatus of Emile and Pierre Thomas, figs. 29 and 30, the sulphur ore is rapidly heated to 130°; and if the operation be repeated ten times a

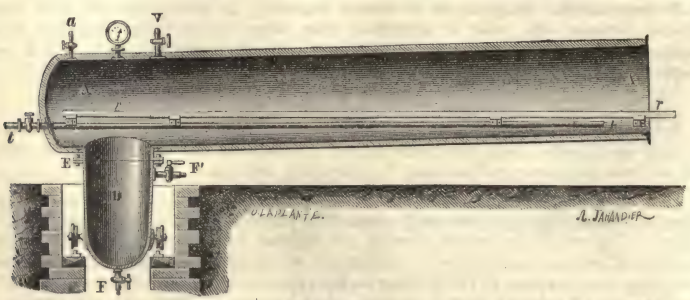


FIG. 29.

day, as much ore can be worked up in a comparatively small space, without loss of sulphur and formation of sulphurous acid, as in a calcarone of 14,000 cubic feet capacity. The sheet-iron cylinder (A), about 3 feet in diameter, contains a tramway (*r r*), upon which a truck laden with ore can be pushed over the vertical cylinder (D). After running in the truck, the cylinder (A) is hermetically closed, and steam, having a tension of from 4 to 5 atmospheres, is passed through the pipe (*t t*), whence it escapes in fine jets, through a number of small holes. By opening the cock (*a*), the air contained in the apparatus at the beginning of the operation is driven out, and when that is closed any remaining air, together with the steam, is allowed only a narrow exit by the cock (F). In case a stoppage should occur at F, the discharge can take place at F'. The temperature in the interior of the cylinder rises rapidly to 130°, the pressure being indicated by the gauge (S). The sulphur melts and flows through the perforated sides of the truck into the conical leaden vessel (D') underneath

(fig. 30). Within an hour and a half the operation is completed, and the steam is transferred from the first cylinder, through the cock V, into a second cylinder, from which it expels the air, and at the same time serves to heat it. The receiver (D D), furnished with wheels, being then detached and let down upon a tramway, placed at no great distance beneath, is run into the magazine, where the leaden cone D′ is emptied of its contents. The trucks, containing the exhausted residues, are then drawn out, and recharged with fresh ore.

At many places where the sulphur ore is rich, the sulphur is simply melted in pans (B, fig. 31), made of cast iron, the mass being heated to 120° or 150°. In this

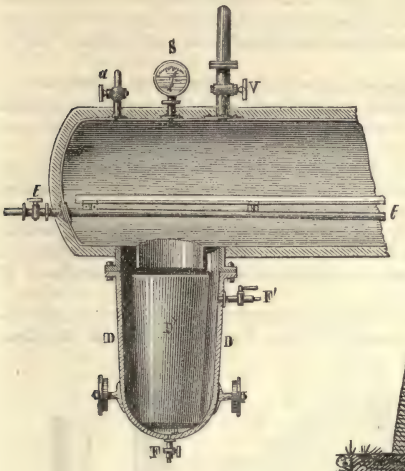


Fig. 30.

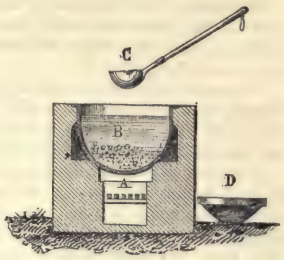


Fig. 31.

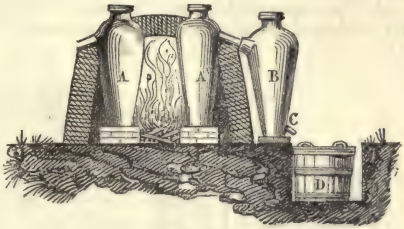


Fig. 32.

case, a rise of temperature to 250° must be avoided, for at that temperature sulphur becomes thick and viscous. After the impurities have been deposited, the sulphur is removed by means of the ladle (C), and poured into a vessel ready at hand, made of wood or sheet iron.

The earthy residues, deposited from the molten sulphur, are sometimes worked in another way for the further extraction of sulphur.

Extraction by Distillation.—The distilling apparatus admits of the working of an ore containing only about 12 per cent. of sulphur. This apparatus consists of large crucibles (A A, fig. 32), of which from 12 to 16, in a double row, stand together in a furnace in such a way that between the two rows there is room for fuel. Each crucible is charged with 50 pounds of ore, and the mouth of the crucible is closed with slabs of fire clay, smeared with loam. A delivery pipe conducts the sulphur vapour into a second crucible or receiver (B), where it condenses, the liquid sulphur flowing through the opening (C) into the vessel (D) beneath. Twelve crucibles, which contain together 600 pounds of raw material, require for fuel about 140 pounds of wood, and they yield in a single operation, which lasts 7 hours, about 192 pounds of sulphur.

Although in this way distilled sulphur is obtained, it is never quite pure, since the boiling of the sulphur causes impurities to be carried over with the sulphur vapour. This sort of raw sulphur contains from 3 to 10 per cent. of impurity.

The amount of impurity in sulphur may be easily estimated. A small weighed portion is submitted to distillation, and the weight of the distilled portion, consisting of pure sulphur, or that of the residue, is ascertained, or both.

The production of raw sulphur in Sicily is very large, in spite of its imperfections. According to Payen, Sicily exports annually about 200,000 tons of sulphur.

The raw sulphur obtained by any of the operations described above is generally far from being pure, as will be seen by the following analyses:—

	1	2	3	4	5
Sulphur (sol. in CS_2) . . .	90·1	96·2	91·3	90·0	88·7
Carbonaceous material . . .	1·0	0·5	0·7	1·1	1·0
Sulphur (insol. in CS_2) . .	2·0	—	1·5	2·1	1·7
Siliceous substances . . .	2·3	1·5	3·3	2·8	5·5
Limestone (and celestine) . .	4·1	1·8	2·5	3·0	2·1
Loss	0·5	—	0·7	1·0	0·3

Refining.—The object of refining raw sulphur is the removal of earthy substances mechanically intermixed with it, as well as those bodies which, like sulphur itself, are volatile. The separation of these latter impurities, however, is very difficult, and is never completely effected.

These volatile substances are selenium and arsenic, the latter being in many cases very injurious. A further object in refining sulphur is to give it a marketable form. The most common forms in which sulphur occurs commercially are roll sulphur and the fine sublimate called flowers of sulphur.

For the purpose of purifying sulphur, an apparatus was formerly employed similar to that represented by fig. 31 (see p. 95). The raw sulphur was simply re-melted therein, and ladled out after the impurities had subsided. According to an improved method, it was distilled; but the product obtained was still impure. At the present time, both operations of re-melting and distillation are combined, and conducted in a single apparatus. By this means, the sulphur can be obtained either in the form of roll sulphur, or as flowers of sulphur.

An apparatus of this kind, employed in the neighbourhood of Marseilles, whence this branch of industry started, is represented by fig. 33. It consists of two iron

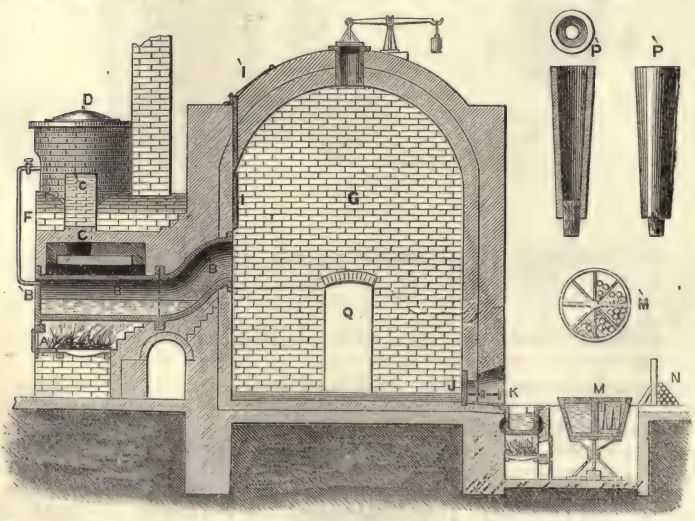


FIG. 33.

cylinders (B) about 5 feet in length, and $1\frac{3}{4}$ feet in diameter, which can be closed in front by means of an iron plate (B′) 3 feet in length. The whole apparatus is set in fire brick. Underneath the cylinder (B) is a fire-place (A), suitable for firing either with coal, wood, or turf. The flame plays first under the cylinder (B), and then, by means of the flue (c c), under the vessel (D), in which the sulphur is melted. This melting vessel, 3 feet in diameter, and 3 feet in height, can be shut by means of a lid, and communicates with the cylinder (B) by means of a cock and the pipe (F). The cylinders (B) open into the brick chamber (G) through connecting pieces (B″). By means of a slide (I), moved by the rod (I′), the aperture at B″ can be opened and shut at pleasure. The brick chamber is about 23 feet long, 16 feet deep, and 7 feet high, having a capacity of about 2500 cubic feet. At one end is a door (Q), made of sheet iron, covered with lead, and externally closed with light brickwork serving to

admit a workman into the chamber. At the lower part of one side of the chamber is an opening, closed by a cast-iron plate (J), having in it a hole $\frac{1}{2}$ inch in diameter. A moveable rod (K) fits into this hole, so as not only to shut it, but also to allow of the size of the aperture being regulated. In order to have more command over the movement of the rod, there is a screw attached to it, which works in a cross piece, built in on both sides. The melted sulphur, flowing through the opening at (J), falls first on an inclined plate of cast iron, and then into the vessel (L), below which is a furnace. Near this furnace is a revolving tube (M), divided by partitions into six or eight parts. N is a stand for holding the sulphur sticks.

This combined process of purifying raw sulphur by re-melting and distilling has not yet been introduced in many places; but at Rosenau, in Silesia, the raw sulphur is heated in iron cauldrons, and the vapour given off is condensed in clay receivers.

At Alsattel, in Bohemia, sulphur is distilled from iron retorts, and collected in receivers of the same metal.

Roll Sulphur.—When the apparatus, represented by fig. 33, is employed for the manufacture of roll sulphur, the following method is adopted. For the first operation, both the cylinders (B) are charged each with 6 cwts. of raw sulphur, as dry and free from impurity as possible, and closed by means of the luted lid (B′). The two retorts are not heated at once, but one after the other; the second one being heated when the distillation in the first is half completed. The hot air from the furnace passes through C C to the cauldron (D), which is charged with about $\frac{3}{4}$ of a ton of sulphur. Here the sulphur is melted, and undergoes a preparatory purification, the water evaporating, while the lighter mechanical impurities, such as wood, etc., float on the surface, and the heavier admixtures, such as sand, pyrites, limestone, etc., sink to the bottom.

As soon as the distillation in the first cylinder is completed, melted sulphur from D is allowed to flow through a pipe (F) into the retort (B), thus charging it afresh. By the sinking of the level in the cauldron (D), the workman judges when enough has run out for a charge. The cock is then closed, the pipe removed, and the hole in the lid (B′), through which it passed, is closed with a plug of burnt earthenware.

During the operation, the hot expanded air escapes through a safety-valve made of metal plate, kept nearly in a state of equilibrium by means of a weight, so that any pressure likely to damage the walls is prevented.

Each distillation lasts eight hours, and every alternate four hours one of the cylinders is charged. In this way $1\frac{3}{4}$ tons of raw sulphur are distilled from the six charges worked in twenty-four hours. By this continuous distillation, the chamber is kept continually at a temperature higher than the melting-point of sulphur; so that sulphur condenses there in the liquid form. As soon as the level of melted sulphur in the chamber has risen to the height of twelve or eighteen centimetres, the cock (K) is opened, and the sulphur is allowed to flow into the vessel (L), which has been previously heated; while a workman ladles it continually into the moulds (P P′), made of boxwood (which are shown on a magnified scale in fig. 33).

In order that the work of casting may be continued without interruption, a child takes the filled and cooled moulds from the tub (M and M′, fig. 33), empties them, and hands them to the caster, who fills them again, and places them in the partitions containing water. In this manner one division after the other is filled, and during the time required for cooling down others are filled in the same manner.

In order to remove the sticks of sulphur from the moulds, the somewhat conical plug at the bottom of the mould is pushed upwards, whereupon the sulphur sticks, which have undergone some contraction in cooling, easily fall out upon inverting the mould. They are piled upon the stand (N), and are there thoroughly cooled down.

The sulphur, when freshly cast, is semi-transparent, of a colour varying from yellow to orange, but it gradually becomes opaque and assumes the ordinary light yellow colour.

Roll sulphur is generally exported in casks of soft wood, lined with white paper.

Flowers of Sulphur.—When the vapour of sulphur is rapidly cooled down to a temperature below the melting-point of sulphur, it condenses in the form of a powder, consisting of small microscopical crystals called flowers of sulphur.

In preparing flowers of sulphur the apparatus employed is the same as that used in the production of roll sulphur (fig. 33). The temperature of the chamber, however, must not rise higher than 111°, so as to avoid the melting of the sulphur. In order to accomplish this, only two distillations are carried out within twenty-four hours, and the charge for each distillation is only 3 cwts. of raw sulphur. With such slow distillation the temperature of the chamber never reaches the melting point of sulphur, and the flowers of sulphur retain their form.

As soon as the layer of condensed flowers of sulphur has attained a height of 20 or 24 inches, the door is opened and the sulphur raked out.

The dry flowers of sulphur are packed either in casks lined with paper or in sacks of stout linen.

It is evident that flowers of sulphur must always have a slightly higher price than roll sulphur, seeing that the preparation requires more time.

The fine division of flowers of sulphur augments the inflammability of the material, and renders it more suitable for mixing than roll sulphur. But it is less pure than roll sulphur, containing more moisture, together with a small quantity of sulphuric and sulphurous acids, and even traces of hydrocarbons. Flowers of sulphur may, however, be easily purified by washing with water, and drying.

On account of its greater purity, roll sulphur is preferred even in the manufacture of gunpowder, for which purpose it has first of all to be powdered.

The use of flowers of sulphur as a remedy for the disease of the vine has considerably increased of late, and it has caused experiments to be made with the object of avoiding loss and other disadvantages in the preparation. Favourable results were obtained by enlarging the surface of the distilling apparatus, and the cubic contents of the condensing chambers.

The improved apparatus of Dujardin and Bailly is represented by figs. 34 and 35.

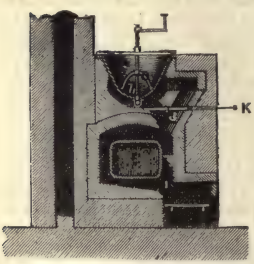


Fig. 34.

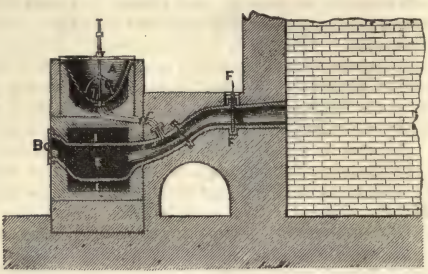


Fig. 35.

The cast-iron distillatory vessel (E) is considerably expanded in the middle, and it ends in two contracted necks, bent upwards, one of them being generally closed with a lid (B), while the other conducts the sulphur vapour into the chamber.

The arrangement of the fire-place (I I) protects the distilling vessel from direct contact with the flame, and from becoming too strongly heated. The gases of combustion play first round the distilling vessel (E), and pass through a flue (J) under the cauldron (A) in which the raw sulphur is melted, or into the chimney, according to the position of the damper (K), and the heavy mechanical admixtures are deposited in the annular gutters at C. The valve (*b*) being opened, the melted sulphur flows through a pipe (*d*) into the distilling vessel, and the charging of the distilling vessel is effected without the use of the movable pipe necessary in the apparatus previously described.

The slide (F F′) serves to interrupt the communication of the distilling vessel with the chamber, so that the latter may be entered for the purpose of removing its contents. This chamber differs only in size from that of the older system; it is 40 feet long, 33 feet wide, and 16 feet high, thus having a capacity of more than 20,000 cubic feet.

The distilling vessel (E) has sectionally (fig. 34) a height of 21½ inches and a breadth of 32½ inches. Its length is 6 feet 4 inches. Accordingly, this distilling vessel is much larger than the old one, and can receive at each charge ¾ of a ton of sulphur. With this apparatus, the rate of production is doubled, and the cost of working is less than with the old one.

A considerable improvement of this apparatus consists in giving the distilling vessel an elliptical shape, and conducting the hot air from the furnace, first over the upper part of the distilling vessel, which must be surrounded with fire clay, and then under it into the flue, either directly or after passing underneath a cauldron for melting sulphur.

Figs. 36 and 37 represent two vertical sections, and fig. 38 a horizontal section of the apparatus. B B″, roasting and fire room; C″ C, flue through which the hot air passes, either direct into the chimney, or is conducted underneath a cauldron (E); A is the distilling vessel, having a diameter of 5½ feet and a depth of 18 inches. The mouth, 9 in. wide and 11 in. deep, is closed with a lid by means of a cross bar. The pipe of the distilling apparatus, which leads into the chamber, is 2½ feet in width and 17 in. deep. The pipe (H), through which the melted sulphur flows into the distilling vessel, has 8½ in. diameter; the elliptically-shaped preparatory heating cauldron (E) has

at its widest part a diameter of 3½ feet; and at its narrowest a diameter of 26 in. and a depth of 3¼ feet.

If a chamber of 10,000 cubic feet capacity is connected with an apparatus of the kind for refining raw sulphur, where there are two distilling vessels, each of which

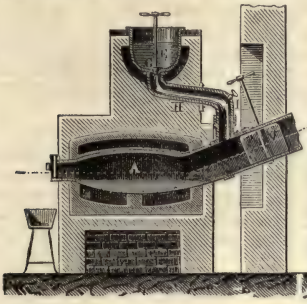


FIG. 36.

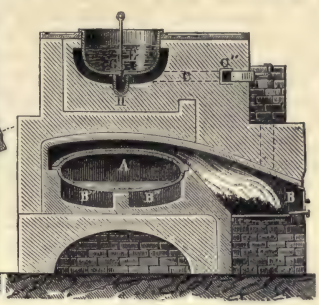


FIG. 37.

can be charged with 12 cwts. of raw sulphur every twenty-four hours, it is possible to work up 4¾ tons in this space of time. If, however, a chamber of the same capacity be adapted for the production of flowers of sulphur, nearly 2½ tons of manufactured product will be obtained in twenty-four hours.

Considering the causes which have led to the various changes in the refining apparatus in use since 1825 (the date of the introduction of the process of distillation by Michel in Marseilles), it is obvious that all improvements aimed at diminishing the depth of the distilling vessel, increasing the surface of the liquid sulphur, and raising the temperature of the upper part of the distilling vessel. Deep boilers were changed for cylinders, the latter for slightly curved retorts; and finally an elliptical distilling apparatus has been employed. These alterations are closely connected with the circumstance that the latent heat of sulphur vapour is so inconsiderable that in the older forms of apparatus a large portion of the sulphur vapour was condensed upon the surface of the boiling sulphur, and falling back into it had to be evaporated again. In this way there was much loss of time and fuel, which has been avoided as far as possible in the newer constructions.

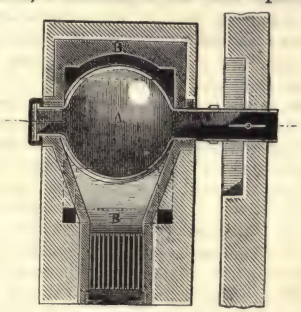


FIG. 38.

EXTRACTION FROM PYRITES.—The extraction of sulphur from iron pyrites is advantageous only in districts where wages are low, and fuel and ore are both cheap and abundant. The process was originally introduced into France by Dartigues, at the time of the French Revolution, when France was no longer able to obtain sulphur from Sicily.

The composition of iron pyrites is represented by the formula FeS_2, and it contains 53·33 per cent. of sulphur, of which about one-half, or 26·66 per cent., is capable of being driven off by strongly heating the ore. In order, however, to get as much sulphur as this from iron pyrites, it would be necessary to heat it to a temperature high enough to melt the residue, and that would soon destroy the fire-clay cylinders. The iron pyrites is, therefore, only heated enough to drive off from it 13 or 16 per cent. of sulphur, and then the residue, not being fused, can be more easily removed from the retort.

The operation is conducted in furnaces, in which conical retorts of fire clay are placed in an inclined position in rows over each other. The narrow ends of the retorts project outside the furnace, and communicate with a pipe extending along the front; the opposite ends also projecting a little beyond the furnace on the other side serve for charging the retorts with pyrites, and can be closed with lids. Upon heating the retorts, the sulphur condenses in the anterior part, and flows into the common condenser. At one time, instead of a common condenser, and in some places it is even now the case, the mouth of each retort was connected with a vessel filled with water into which the sulphur dropped. Each retort is charged with ½ cwt. of pyrites.

In some parts of France sulphur is extracted from iron pyrites in shaft furnaces which resemble lime kilns.

According to Mène, a continuous working kiln, which is in use in Sweden, deserves especial notice. The pyrites is placed in a kiln somewhat like that used in burning lime, but terminating above in a flue, at first inclined, and finally horizontal, where the sulphur is condensed. The kiln charged with pyrites is set fire to with wood and turf, the further heating taking place at the cost of the burning pyrites itself. In proportion as the exhausted pyrites is removed from a side opening below, fresh pyrites is thrown in from above. By means of this kiln, according to Mène, one half of the sulphur contained in iron pyrites is extracted, while only about one third is extracted when fire-clay retorts are employed.

It may here be mentioned that it has often of late been attempted, and with partial success, to obtain sulphur from iron pyrites indirectly. For this purpose the iron pyrites is burnt, and the sulphurous acid thus formed is either made to pass over red-hot charcoal, or coke, or it is in some cases reduced by means of sulphuretted hydrogen. In all cases the residue obtained in distilling sulphur from pyrites can be converted by oxidation into ferrous sulphate and worked up for green vitriol either directly or after a supplementary roasting.

In Sweden, and in the Harz, sulphur is obtained as a by-product in roasting copper pyrites, or ores containing galena.

Sulphur from Soda Waste.—After attempts had been made for a long time to utilise soda waste, which contains a considerable amount of sulphur, and obtain the sulphur from it, success was at last achieved in 1863 by Mond, and shortly after him by Schaffner, both of whom devised methods which have been employed of late on a large scale (*vide* 'Soda Manufacture').

Schaffner's Process. Soda waste contains a compound of calcium sulphide with lime, from which polysulphurets of lime and hyposulphite of lime are formed when such waste is permitted to lie in heaps in the air for a long time. When the mass is lixiviated with water, these lime salts are dissolved. The liquor thus obtained is heated and decomposed with hydrochloric acid, which precipitates part of the sulphur, while another part escapes in the form of sulphurous acid. In order not to lose the sulphurous acid, it is passed into a second vessel containing fresh liquor, and re-acting upon the polysulphurets, the sulphur of both compounds is precipitated at the same time. The precipitated sulphur is washed, and melted under pressure in iron boilers with water and a little caustic lime, by means of steam, and is then cast into moulds. The sulphur, obtained by this process, has the same degree of purity as roll sulphur. This method of recovering sulphur from alkali-makers' waste is chiefly adopted in Germany; in this country, as well as in France, the process of Mond has been introduced into most large manufactories. This process also depends upon the partial oxidation and precipitation of the sulphur with hydrochloric acid. It differs, however, from the method proposed by Schaffner in practical details.

Besides these methods, there are a number of others, according to which the sulphur of soda waste is first of all converted in part or entirely into either sulphurous acid or into sulphuretted hydrogen, and is precipitated from these compounds in the free condition.

Sulphur has been obtained of late from the by-products of the purification of coal-gas by means of ferric hydrate; also from sodium sulphide; and finally from the gases containing sulphurous acid produced in roasting blende.

Uses.—Raw sulphur is employed in the manufacture of sulphuric and sulphurous acids and of sulphuretted hydrogen; and, generally speaking, nearly all the artificial compounds of sulphur are either directly or indirectly obtained from raw sulphur.

Refined sulphur is used in the preparation of lucifer matches; on a large scale in the manufacture of gunpowder and blasting powder, and in pyrotechnics. The use of sulphur for the above purpose is owing to its property of igniting at a temperature of 250°.

Owing to the fusibility of sulphur, and its readily assuming the liquid state at a temperature between 111° and 140°, sulphur is especially adapted for taking casts of medals, etc. As it easily combines with metals, it is employed in the preparation of a number of metallic sulphides, such as those of mercury (artificial cinnabar), copper, iron, etc. It serves further in the preparation of various lutes. An iron cement, which, owing to the formation of basic ferric sulphate, hardens in contact with the air, is obtained by mixing 100 parts by weight of iron filings with 3, 5, 10, or 20 parts by weight of flowers of sulphur, and from 3 to 5 parts by weight of sal-ammoniac, and kneading the mixture with water. This cement is used chiefly for filling in between the joints of steam boilers, for cementing together iron pipes, etc.

When caoutchouc is treated with sulphur in a state of solution, it absorbs from

one to two per cent., yielding vulcanised india-rubber, a very elastic mass, which retains its elasticity at a low temperature, and does not stick like pure caoutchouc. This kind of caoutchouc has recently been extensively employed; and the branch of industry to which it has given rise will be detailed in a later chapter.

Coarse linen dipped in melted sulphur becomes coated with it. In this way are prepared the sulphurated or quick matches, used for burning in the inside of moist casks and vats, so as to produce sulphurous acid, which serves for preventing too violent fermentation, or the decomposition of easily decomposable liquids. Thus, for instance, casks intended for the reception of wine or beer are 'sulphured' before these liquids are put into them. In the same way blood may be preserved, and many boiled leguminous plants. Sulphuring with burning sulphur serves also to destroy noxious insects in feathers or corn; to remove fruit stains from linen; and on a large scale for bleaching silk, wool, gut strings, straw hats, isinglass, sponge, etc. Bleaching with the gas of burning sulphur or sulphurous acid is conducted in well-closed round chambers, about 16 feet high, and with a capacity of about 3600 cubic feet; they are entirely filled with the articles that are to undergo the bleaching operation. These articles, previously washed with soda and soap and water, and pressed, are then in a still moist condition hung out in rows upon wooden supports in the bleaching chamber, in such a manner that a space of about ½ an inch is left between each row. Sulphur sufficient to yield the sulphurous acid required is then burnt in all four corners of the chamber.

Chimney fires can be extinguished by means of sulphur. Sulphur is thrown upon the fire and the draught cut off, and thus the chimney gets filled with gaseous sulphurous acid which extinguishes the fire. Powders for extinguishing fire also contain sulphur, which, owing to the formation of sulphurous acid, suffocates the flame.

According to Heeren, Bucher's powder for extinguishing fire has the following percentage composition:

Nitre	66
Sulphur	30
Charcoal	4

A solution of sulphur in linseed oil is used for impregnating gypsum casts, building stones, etc.

The use of flowers of sulphur as a remedy for the disease of the vine, produced by a peculiar fungus, the *Oïdium Tuckeri*, or Erésiphe, which is especially prevalent in the south of France, has caused a considerable increase in the consumption of this article. The fungus is destroyed by dusting the vines with flowers of sulphur, which operation is performed, 1, before the flowering, 2, during the flowering period, and 3, when the fruit begins to form. In hot-houses, the same effect may be produced by strewing the heating pipes with flowers of sulphur.

Flowers of sulphur have been found to act equally efficiently in the analogous diseases of the peach tree, the rose tree, and the hop, which are caused by similar fungi.

In order to distribute the sulphur equally over all the infected parts of the plants, various forms of apparatus have been employed. One of them, which was in general use up to 1856, introduced by a gardener of the name of Goutier, had the form of a

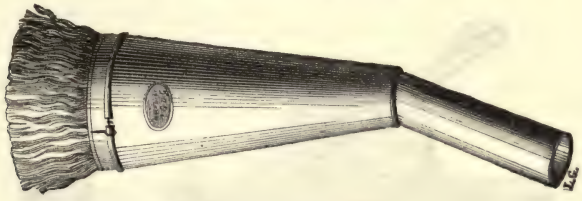


Fig. 39.

bellows. Since then, Ouin and Frank have introduced an apparatus, simple in its construction, and cheaper, the so-called *boîte à houppe* (tarsel box), which is represented by figs. 39, 40, 41 and 42. It consists of a conical tube of tin plate, which, as fig. 42 shows, is filled to one-half with flowers of sulphur, or about one pound. The upper portion, which forms the characteristic feature of the apparatus, consists of a movable lid. The lid is furnished with five rows of woollen wick fastened in concentrical rings of metal plate by means of fine wire, and between the rows of wick are concentrical

openings, as shown by fig. 40. Inside the tube, at about three-fourths of its length, there is a cross of fine bands of tin-plate which serves to loosen any sulphur that may have got conglomerated together.



FIG. 40.



FIG. 41.

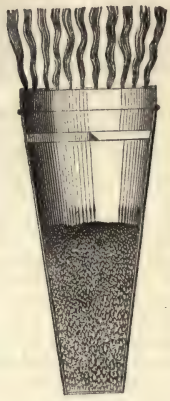


FIG. 42.

Upon shaking the box, the sulphur passes through the openings between the rows of wick, and becomes thereby so finely divided, that it covers with a fine dust all parts of the plant operated upon. Not even this fine division of the sulphur would, however, suffice, were it not that a part of it evaporates under the influence of the sun's rays, the volatilised portion settling on other parts of the plant. If a still greater distribution of sulphur be required, wicks of horse-hair are employed in the place of the woollen ones. When the tarsel box is used for dusting the tops of tall vines or trees, it is furnished with a long handle (fig. 39).

On account of the high price of flowers of sulphur, it has been attempted to make use of powdered sulphur, but it is not at present certain whether this has the same effect. According to Payen, good results have been obtained with flowers of sulphur; while, on the other hand, vine-dressers often give powdered sulphur the preference, probably, however, on account of its being cheaper.

Owing to flowers of sulphur being dearer than powdered sulphur, they are often adulterated with the latter, which can, however, be easily detected by means of the microscope. When examined under the microscope, flowers of sulphur, when unadulterated, are found to consist of small crystals, or groups of crystals; whereas, when they contain powdered sulphur, this is recognised by its irregular angular structure. Another way of detecting this adulteration is the following. Five grams of the sulphur to be tested are placed together with 25 c.c. of ether in a cylindrical glass

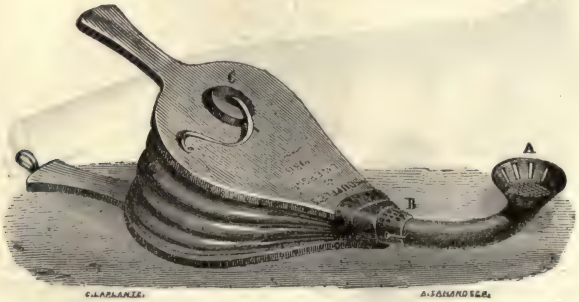


FIG. 43.

jar of 25 c.c. capacity, graduated into 100 equal parts, and shaken together, and then allowed to stand quiet for some time. If the flowers of sulphur are pure, the sedi-

ment which is formed after standing occupies a greater volume (50–60 grad.) than is the case when powdered sulphur alone is treated in like manner; the sediment in the latter case occupying a volume of about 24–40 grad.

Sulphur may be spared and labour reduced by using a bellows without valve, as constructed by Lavergne, represented by fig. 43. Finely-divided sulphur is introduced at c, gets agitated by the inflowing air, and is thrown out again at A each time the bellows is pressed, forming a cloud of sulphur dust.

By means of this apparatus, a labourer is able to distribute 22 lbs. of sulphur in 7 hours, five times this quantity sufficing for 2 acres of land. As has already been mentioned, the dusting is performed three times, shortly before, during, and shortly after the flowering period.

The wine must produced from vines that have been sulphured always gives an indication of sulphuretted hydrogen. The sulphuretted hydrogen, however, disappears during the fermentation, its sulphur becoming converted into sulphate and dissolved.

Compounds.—Sulphur forms with other elementary substances a large number of compounds which are termed sulphides, and as a class they are very analogous to the oxides in their constitution and chemical relations. Only two oxides of sulphur are known, the dioxide or sulphurous oxide SO_2, and the trioxide or sulphuric oxide. Both of these substances combine with water, and with basic oxides, forming two series of salts termed sulphites and sulphates, the respective hydrogen salts being sulphurous acid H_2SO_3 and sulphuric acid H_2SO_4.

Besides these oxygen compounds of sulphur there are several other series of analogous compounds of sulphur with oxygen and hydrogen or metals. The composition of the hydrogen compounds or acids is given in the following table:—

Hyposulphurous acid	H_2SO_2	Trithionic acid	$H_2S_3O_6$
Thiosulphuric acid	$H_2S_2O_2$	Tetrathionic acid	$H_2S_4O_4$
Dithionic acid	$H_2S_2O_6$	Pentathionic acid	$H_2S_5O_6$

Sulphides are classified like oxides according to the atomic proportions of sulphur they contain, as monosulphides, disulphides, etc.

The sulphides of the metals are solid substances which are generally insoluble in water, except the sulphides of the alkali metals. Some of them melt more readily than the corresponding oxides; some are partially and others entirely decomposed by heating, and a few are volatilisable. The sulphides as they occur naturally are often crystalline, brittle, and dark-coloured, and several of them have a metallic lustre. Many of the sulphides are, like oxides, capable of combining together and forming saline compounds termed sulpho-salts, which are analogous to oxy-salts; the sulphides of the metalloids having the characters of acid sulphides, and those of the metals having generally the characters of basic sulphides. Thus potassium sulphsenite K_3AsS_3 corresponds to the oxyarsenite K_3AsO_3.

Hydrogen monosulphide H_2S, commonly called sulphuretted hydrogen, corresponds to water, and it forms compounds with other sulphides, which are called sulphydrates, and are analogous to the oxyhydrates; as, for instance, potassium sulphydrate KHS, corresponding to the hydrate KHO.

Many sulphides and sulpho-salts occur naturally as minerals, and are of great technical importance, as the principal sources from which several metals are obtained.

Carbon disulphide CS_2, corresponding to carbon dioxide CO_2, combines with basic sulphides forming salts called sulpho-carbonates, which correspond to carbonates but contain sulphur in place of oxygen:—

Calcium carbonate	$CaCO_3$
,, sulpho-carbonate	$CaCS_3$

Sulphur forms several compounds with phosphorus, iodine, bromine, and chlorine, but the only one of these compounds that is used for industrial purposes is the chloride S_2Cl_2.

SULPHUROUS OXIDE.

Formula SO_2. Molecular Weight 64.

History.—This substance, commonly called sulphurous acid, was long known as the gaseous product into which sulphur is converted when it is burnt: but its composition was not ascertained until the latter part of the last century.

Occurrence.—Sulphurous oxide does not frequently occur naturally; it is present in the gaseous exhalations of volcanic districts, and more rarely in the water of some mineral springs.

Composition.—Sulphurous oxide consists of equal weights of sulphur and oxygen; it contains its own volume of oxygen and half its volume of gaseous sulphur, the joint volume being reduced one-third in the combination.

Characters.—Sulphurous oxide is at the ordinary temperature a colourless gas having a strong suffocating odour. Its density is 32 relatively to hydrogen, and its specific gravity as compared with air 2·247. It condenses at a temperature of −10° to a colourless liquid having a specific gravity of 1·490 as compared with water. When the liquid is evaporated, it absorbs a large quantity of heat, causing a very speedy reduction of the temperature of the surrounding atmosphere. This property of liquid sulphurous oxide is taken advantage of in laboratories for the production of great cold. If, for instance, liquid sulphurous oxide be poured over the bulb of an alcohol thermometer surrounded with cotton wool, the thermometer sinks to −50° or −60°, while, if a mercury thermometer be used, the mercury solidifies. Chlorine and ammonia gas may be condensed to liquids by passing them through bulb-shaped tubes, surrounded with cotton wool and kept moist with liquid sulphurous oxide.

When liquid sulphurous oxide is evaporated under the air-pump, a thermometer placed in it sinks to −80°, and the non-volatilised portion is converted into a crystalline solid.

Sulphurous oxide is soluble in water, the specific gravity of the water increasing in proportion as the gas is absorbed; consequently the specific gravity of an aqueous solution of sulphurous oxide varies according to the amount of dissolved gas, as shown in the following table by M. Anton:

Specific Gravity	Percentage of Sulphurous Oxide	Specific Gravity	Percentage of Sulphurous Oxide
1·046	9·54	1·020	4·77
1·036	8·59	1·016	3·82
1·031	7·63	1·013	2·86
1·027	6·68	1·009	1·90
1·023	5·75	1·005	0·95

At a temperature of 0° water dissolves 68·8 volumes per cent. of sulphurous oxide gas, at 10° 51·4 volumes, and at 20° only 36·2 volumes. This difference in the solubility of sulphurous oxide in water at different temperatures has often caused accidents, which have arisen from hermetically-sealed bottles or tubes being filled with a saturated aqueous solution of the gas at some low temperature. When such bottles or tubes are brought into a room at the ordinary temperature, the sulphurous oxide tends to free itself, and the pressure thus exerted is often great enough either to drive out the stopper or to burst the vessel.

Sulphurous oxide is very useful on account of its action upon nitric acid, which is reduced by it to nitric oxide, a reaction which plays an important part in the manufacture of sulphuric acid (*vide* Sulphuric Acid).

Sulphuretted hydrogen and sulphurous oxide mixed together in presence of water undergo a mutual decomposition, water being formed, and sulphur eliminated; but the decomposition is not complete, and a considerable amount of pentathionic acid is formed, probably according to the following equation:

$$10SO_2 + 10H_2S = 8H_2O + 10S + 2H_2S_5O_6.$$

This decomposition does not take place when the gases come into contact in a dry condition.

A further very important property of sulphurous oxide is its action on vegetable colours, especially so because the common bleaching agent, chlorine, cannot be used for bleaching nitrogenous substances, since silk, wool, feathers, and straw fabrics are rendered yellow by chlorine, and have therefore to be bleached with sulphurous oxide.

Preparation.—There are various methods of preparing sulphurous oxide, the principal of which consist in burning sulphur or some metallic sulphide, and in the reduction of sulphuric acid. The most important methods are the following:—

By Burning Sulphur.—For the preparation of either sulphurous oxide, or of aqueous solutions, or lyes containing sulphurous acid in combination with potassium, sodium or calcium, the apparatus shown in fig. 44 (p. 105) may be employed:

Sulphur is burnt in a vessel of sheet metal on the hearth of a furnace A. The hot sulphurous oxide passes through a kind of chimney into the condensing tube (B B'), and from thence through C into a long leaden vessel (B''), the bottom of which is sloping, and the interior is fitted with partitions (d' d'), in the manner shown in horizontal projection, fig. 45. This receiver is closed with a lid, kept cool by water

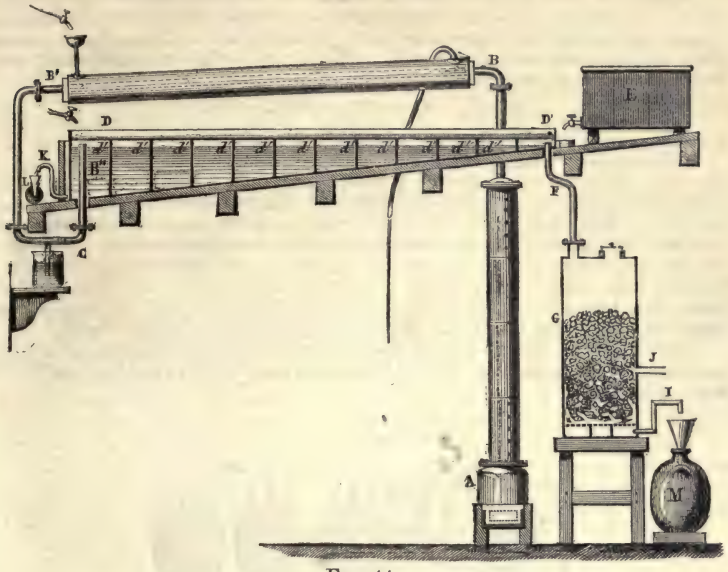


FIG. 44.

trickling over it. The liquid, consisting either of water or of a solution of potash, soda, or lime, flows from the reservoir (E) into the upper part of the absorption chamber, and from thence into the other divisions successively, escaping eventually through the tube K and the pipe L. The sulphurous oxide, entering at the lowest division, passes in the contrary direction, indicated by the arrows (fig. 45), escaping finally through F,



FIG. 45.

which is connected with a vessel (G) filled with moist soda crystals, so as to absorb any free gas. The soda retains the last traces of sulphurous oxide, the carbonic acid thus liberated escaping through the tube (J) into a chimney.

The sodium sulphite thus formed is more soluble than sodium carbonate, consequently when the mixture is treated with water it passes through the perforated bottom of the vessel *g*, and the pipe I into the receiver M.

When lime is used in the place of soda, the apparatus is fitted with a contrivance for stirring the lime.

For the preparation of solutions of sulphurous acid in water, Calvert recommends the use of a tower about 40 feet high and 4 feet wide, filled with pieces of pumice, into which the gas is conducted from below, a moderate stream of water being permitted to trickle through the pieces of pumice from above.

For the method of preparing gaseous sulphurous oxide for bleaching purposes, and in the manufacture of sulphuric acid, see p. 101 and the article 'Sulphuric Acid.'

By Reduction of Sulphuric Acid.—Although this method of preparing sulphurous oxide is decidedly more expensive than that just described, it is still sometimes employed.

The deoxidation of the sulphuric acid is effected by various substances, of which the principal are charcoal, metals, and sulphur.

By Charcoal.—An apparatus for the reduction of sulphuric acid is represented by fig. 46. It consists of two or three balloons (A), of glass or stoneware, fitted into a furnace, and heated from beneath by means of a sand bath. The balloons are half filled with charcoal and concentrated sulphuric acid, which mixture yields, when heated, carbonic acid, water, and sulphurous oxide, according to the equation:

$$2H_2SO_4 + C = CO_2 + 2H_2O + 2SO_2.$$

A small quantity of carbonic oxide is formed in this reaction.

The larger proportion, however, of the gases consists of carbonic dioxide and sulphurous oxide, which are passed through a wide delivery tube into three receivers, similar to Woulfe's bottles in shape and arrangement. These receivers are filled with water to a third or half their height; the first serving to retain any sulphuric acid carried over with the gas, the two others for the absorption of sulphurous oxide. The carbon dioxide escapes into the air through c'. As soon as the water in the receivers is saturated with sulphurous oxide, the solution is drawn off by cocks placed a little above their bottom. The receivers can, of course, be charged with alkaline solutions instead of water, in which case the corresponding sulphites would be formed.

Retorts may be advantageously used in the place of balloons for heating the mixture of sulphuric acid and charcoal, being like them filled to one half, and heated in the same way.

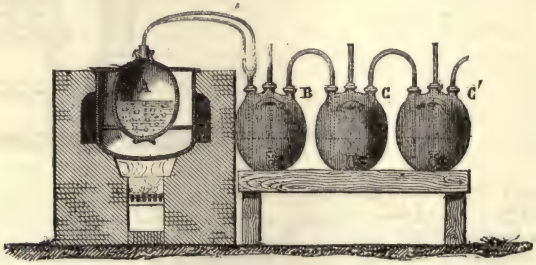


Fig. 46.

Reduction of Sulphuric Acid by Metals.—The preparation of sulphurous oxide by reducing sulphuric acid with metals is chiefly employed on a small scale in chemical laboratories. The most suitable metal for the purpose is copper, which reacts upon sulphuric acid according to the equation:

$$2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2.$$

Copper turnings (dirty scraps may also be used) are brought into a capacious glass flask or retort, and covered with from two to three times their weight of concentrated sulphuric acid. The generating vessel being connected by means of glass tubes with a Woulfe's bottle containing water, and this with another vessel containing some liquid for absorbing the sulphurous oxide, the mixture of copper and sulphuric acid is heated gradually over a sand bath up to the boiling point of sulphuric acid. When this point is attained, a development of sulphurous oxide gas begins, which continues so long as undecomposed copper and sulphuric acid are present in the generator. A stronger heat towards the end of the operation is advisable.

Reduction of Sulphuric Acid by Sulphur.—When six parts of sulphuric acid are heated together with one part of sulphur a very strong development of sulphurous oxide takes place, according to the equation:

$$2H_2SO_4 + S = 3SO_2 + 2H_2O.$$

The reaction is, however, often so violent that for the preparation of sulphurous oxide on a small scale, the reduction of sulphuric acid by copper is preferable.

Instead of sulphuric acid, sulphates may be used for preparing sulphurous oxide. Thus, according to M. Stolba, sulphurous oxide in a state of great purity may be obtained by heating together four parts of anhydrous ferrous sulphate (green vitriol) and one part of sulphur.

Copper sulphate (blue vitriol) may be also employed for preparing sulphurous oxide in the above way.

Manufacture of Sulphurous Oxide from Pyrites.—When iron pyrites or other metallic sulphides are heated in contact with air, a process which is technically termed roasting, the sulphur is oxidised to sulphurous oxide (less often to sulphuric acid) and the metal to its oxide, part of which combines with the acid. The sulphurous oxide set free in this process was formerly allowed to escape into the atmosphere, a plan not only involving waste of a valuable substance, but also at the same time the destruction of all vegetation in the vicinity. This sulphurous oxide is now collected and used for the preparation of sulphuric acid in lead chambers; some sulphuric acid manufacturers indeed employing pyrites alone as the source of sulphuric acid. The following formula will serve to explain the roasting process:

$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2.$$

A further method of obtaining sulphurous oxide may be mentioned, which consists in heating to redness, in fire-clay retorts, an intimate mixture of 4 parts of sulphur with 6 parts of manganese peroxide. The decomposition takes place according to the equation:

$$2S + MnO_2 = MnS + SO_2.$$

A small quantity of manganese oxide always remains behind mixed with the sulphide, which is owing to portions of manganese getting heated to redness without coming into contact with sulphur.

Sulphurous oxide occurs also as a by-product in a number of industrial operations; as for instance in the manufacture of glass; in the preparation of ultramarine, when Glauber's salt is employed; also in the saponification of soap with sulphuric acid for separating the stearic acid, in burning fuel containing pyrites, etc.

Uses.—Sulphurous oxide is extensively used, its most important application being the manufacture of sulphuric acid. Another important application of sulphurous oxide is in bleaching, especially in the case of silk and woollen goods, which cannot be bleached with chlorine, owing to their being rendered yellow by that substance.

Compounds.—Sulphurous oxide combines chemically with water to form hydrogen sulphite, H_2SO_3, or sulphurous acid; but this compound is readily decomposed, and upon boiling a solution of sulphurous acid for a short time the whole of the sulphurous oxide is expelled as gas. There is another compound of the gas with water, having a composition represented by the formula $H_2SO_3 8H_2O$, which is obtainable in the crystallised state by cooling a saturated solution of sulphurous acid to $-6°$, while a current of sulphurous oxide gas is passed through it.

Sulphurous oxide also combines with basic oxides, forming a series of saline substances called sulphites, some of which, such as the alkaline sulphites, are freely soluble in water, while others, like barium sulphite, are only sparingly soluble. These salts are readily decomposed by hydrochloric acid, with evolution of sulphurous oxide gas; they also absorb oxygen from the air, and are thus converted into sulphates.

By passing vapour of nitrogen peroxide into liquid sulphurous oxide there is formed, together with nitrous anhydride, a solid substance having the composition $2NO,S_2O_7$, according to the following equation:

$$2SO_2 + 4NO_2 = 2NO;S_2O_7 + N_2O_3.$$

This substance melts when heated, and volatilises without decomposition; it dissolves in concentrated sulphuric acid without change, and with slightly diluted acid it forms a bulky crystalline substance, probably H,NO,SO_4 (*vide* Sulphuric Oxide, Compounds: and Manufacture of Sulphuric Acid; Chamber Crystals).

SULPHUROUS ACID.

Formula H_2SO_3. Molecular Weight 82.

This substance, which exists in the aqueous solution of sulphurous oxide, can be obtained in a crystalline state by passing moist sulphurous oxide gas through a tube cooled by a freezing mixture, or by cooling a saturated solution to 0°. The crystals melt at a temperature a little above 0°, and decompose giving off sulphurous oxide gas. Most of the reactions of sulphurous oxide in the presence of moisture are really due to sulphurous acid.

In a perfectly dry state, sulphurous acid exerts no action on organic colouring matters, it is therefore necessary in bleaching with this substance to insure the presence of moisture. The way in which the bleaching action takes place is not at

present definitely determined, but there must be at any rate two distinct kinds of bleaching action, for there are vegetable colours, which after bleaching with sulphurous acid, reappear upon treatment with very dilute acids, and again others, which no known re-agent restores. Thus, for instance, the red colouring matter of the rose is completely bleached by sulphurous acid, but reappears upon dipping the rose into very dilute sulphuric acid. On the other hand, the red colouring substance of the beet root, which is also bleached by sulphurous acid, cannot be recovered by any re-agent. In the first case, it is supposed that the bleaching property of the sulphurous acid is due to its forming a colourless compound with the colouring matter of the rose, which can be separated again by a weak acid, while in the other case it is supposed that the bleaching action of the sulphurous acid is due to a decomposition and reduction of the colouring matter.

Some vegetable colouring matters, such as chlorophyll, withstand completely the influence of sulphurous acid.

Sulphurous acid acts as an antiseptic in the case of several organic substances, which property is probably due to its preventing the growth of organic ferments.

Sulphurous acid oxidises very readily to sulphuric acid, and is on this account a powerful reducing agent. Sulphuric acid is formed in an aqueous solution of sulphurous acid, exposed to light and air. For this reason, when it is desired to preserve a solution of sulphurous acid for any length of time in a state of purity, the bottles must be completely filled, and kept in a dark place; it is further necessary to expel, by boiling, the air dissolved in the water, before dissolving the gas.

Sulphurous acid readily deprives substances of oxygen. Thus, for instance, it liberates iodine from iodic acid, reduces permanganic acid, and precipitates silver and mercury from solutions of their salts.

Uses.—Sulphurous acid is used as a disinfectant and deodoriser, as it destroys miasms, and decomposes bad-smelling substances, such as sulphuretted hydrogen, ammonium sulphide, etc. Another use of sulphurous acid, which is not less important than the latter, is for preserving wine, hops, and other substances.

Calvert has recommended the addition of $\frac{1}{100}$ of a 10 per cent. solution of sulphurous acid to sugar juice before boiling in vacuum, for lessening the coloration of the syrup, and for stopping any fermentation that may have set in.

Sulphurous acid is also employed for bleaching starch, cane sugar, malt, etc.

A further use of sulphurous acid which may be here mentioned, is for the preservation of corpses for anatomical purposes. Sulphurous acid that has been treated with an excess of zinc is injected into the corpse, which may be then kept for several days. The effect is not to be attributed to sulphurous acid alone, but also to zinc sulphite and hyposulphite.

SULPHURIC OXIDE.

FORMULA SO_3. MOLECULAR WEIGHT 80.

Characters.—This substance, which is also called sulphuric anhydride, is a white fibrous mass resembling asbestos in appearance; it melts at about 18°, and at a higher temperature it volatilises; the vapour is decomposed at a red heat into sulphurous oxide SO_2 and oxygen gas. In the dry state sulphuric oxide is a neutral substance, and it does not alter the colour of blue litmus paper, or exercise any corrosive action on organic substances, but it attracts water from the atmosphere with great avidity, combining with it and forming sulphuric acid; it also gradually causes the decomposition of organic substances, converting them into water, with which it combines, and carbon, which remains as a finely divided black mass. The specific gravity of solid sulphuric oxide is 1·946 at 13°, that of the melted substance 1·970 at 20°.

Preparation.—Sulphuric oxide may be obtained by heating perfectly dry ferric sulphate, $Fe_2 3SO_4$, in a close vessel connected with a condenser. The decomposition that takes place is represented by the following equation:

$$Fe_2 3SO_4 = Fe_2O_3 + 3SO_3.$$

It may also be obtained by distilling the fuming acid known as Nordhausen oil of vitriol.

Compounds.—Sulphuric oxide combines readily with water, forming hydrogen sulphate, H_2SO_4, or sulphuric acid, which is the representative of a very important series of saline substances called sulphates, containing in the place of the hydrogen of sulphuric acid two atomic proportions of monovalent metals, or one atomic proportion of divalent metals for each molecule of sulphuric oxide.

The sulphates are mostly crystallisable substances; with some few exceptions

they are soluble in water, but some of them dissolve only in very small proportions. Many sulphates occur naturally, and in some instances they have originated from metallic sulphides by oxidation.

Sulphuric oxide absorbs the vapour of nitrogen peroxide, forming a crystalline substance having the composition NO_2SO_3, which, when sufficiently heated, is decomposed into oxygen gas and the same substance that is produced by the action of nitrogen peroxide upon sulphurous oxide (see p. 107). This substance, $2NO,S_2O_7$, is also formed, together with sulphurous oxide, by the action of nitric oxide upon sulphuric oxide, according to the following equation:

$$3SO_3 + 2NO = 2NO,S_2O_7 + SO_2.$$

The crystals sometimes formed in the lead chambers of sulphuric acid works when there is an insufficient supply of steam are closely related to these compounds (*vide* Sulphuric Acid, Chamber Crystals).

SULPHURIC ACID.

Formula H_2SO_4. Molecular Weight 98.

History.—Most probably the Arabian chemist, Geber, who lived in Spain in the eighth century, was the first to prepare sulphuric acid, for it is hardly possible that the 'spirit' which he got by distilling alum can have been anything else. In the twelfth century, Albertus Magnus mentions a spiritus vitreoli romani, which must likewise have been sulphuric acid. Basil Valentin, who lived in the fifteenth century, was the first to describe comprehensively and exactly the different methods of preparing sulphuric acid, but even he considered the sulphuric acid prepared in different ways to be distinct substances. Libavius was the first to recognise the identity of the sulphuric acid prepared according to various methods.

The composition of sulphuric acid was long a matter of doubt. Stahl considered it to be a constituent of sulphur; and Mayow, who lived in the seventeenth century, maintained that sulphur was a constituent of sulphuric acid. It was not until 1777 that Lavoisier established the true composition of sulphuric acid.

Occurrence.—Sulphuric acid seldom occurs naturally in the free state, since it is one of the strongest acids, and readily unites with metallic oxides and other bases. Its occurrence in the free state is therefore limited to volcanic sources. Thus, for instance, according to Boussingault, the water of the Rio Vinagre, a river rising in the Andes, in South America, contains, in addition to hydrochloric acid, about one-tenth per cent. of free sulphuric acid. M. Boussingault calculated that this river brings to the surface daily more than 38 tons of sulphuric acid. The water of some other volcanic springs in the Andes also contains sulphuric acid. Another spring of water, very rich in sulphuric acid, occurs in New Granada. It is a hot spring from a volcano called Paramo de Ruiz, 3800 metres above the sea level, and according to Lewy its water contains upwards of one fourth per cent. of free sulphuric acid. The water has a temperature of 69·4°, and contains free hydrochloric acid as well as sulphuric acid.

Sulphuric acid exists far more abundantly in combination with bases as sulphates. The commonest of these compounds are gypsum (calcium sulphate); heavy spar (barium sulphate); celestine (strontium sulphate); anglesite (lead sulphate); green copperas (iron sulphate); blue vitriol (copper sulphate); and alunite (aluminum and potassium sulphate), etc.

Composition.—Sulphuric acid or hydric sulphate contains more than six tenths its weight of oxygen in combination with sulphur and hydrogen, and its constitution is represented in accordance with the double water type $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$, by the formula $\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$, or as a monohydrate of sulphuric oxide by the formula SO_3H_2O.

Characters.—In its most concentrated state sulphuric acid is a colourless, inodorous, thick liquid of oily consistence, on account of which it is termed oil of vitriol. Its density as compared with water is 1·843. By contact with organic substances it readily assumes a brown colour, in consequence of its powerful dehydrating or carbonising action upon such substances, and the sulphuric acid met with in commerce is often coloured brown in this way by dust or small fragments of straw, etc. It solidifies at a temperature considerably below the freezing point of water, and then melts at 10·5°. The liquid acid commences to boil at 290° and is partially decomposed, giving off some vapour of sulphuric oxide, the temperature of the remaining

liquid rising meanwhile, until at about 338° it becomes constant, and the acid that distils over contains $1\frac{1}{12}$ molecule of water for each molecule of sulphuric oxide.

Sulphuric acid mixes readily with water in all proportions, evolving great heat. On this account water should not be poured into concentrated sulphuric acid; for unless this is done with very great caution the heat evolved may suddenly convert the water into steam, and cause the acid to be thrown about with great violence. In mixing the acid with water, it is therefore always preferable to pour the acid gradually into the water. Sulphuric acid also forms several definite crystallisable compounds with water.

The specific gravity of sulphuric acid decreases in proportion to the amount of water it contains. The following table shows the strength of sulphuric acid of different densities at 15°.

Specific Gravity	H_2SO_4 per cent.	SO_3 per cent.	Specific Gravity	H_2SO_4 per cent.	SO_3 per cent.
1·8426	100	81·63	1·398	50	40·81
1·842	99	80·81	1·3886	49	40·00
1·8406	98	80·00	1·379	48	39·18
1·840	97	79·18	1·370	47	38·36
1·8384	96	78·36	1·361	46	37·55
1·8376	95	77·55	1·351	45	36·73
1·8356	94	76·73	1·342	44	35·82
1·834	93	75·91	1·333	43	35·10
1·831	92	75·10	1·324	42	34·28
1·827	91	74·28	1·315	41	33·47
1·822	90	73·47	1·306	40	32·65
1·816	89	72·65	1·2976	39	31·83
1·809	88	71·83	1·289	38	31·02
1·802	87	71·02	1·281	37	30·20
1·794	86	70·10	1·272	36	29·38
1·786	85	69·38	1·264	35	28·57
1·777	84	68·57	1·256	34	27·75
1·767	83	67·75	1·2476	33	26·94
1·756	82	66·94	1·239	32	26·12
1·745	81	66·12	1·231	31	25·30
1·734	80	65·30	1·223	30	24·49
1·722	79	64·48	1·215	29	23·67
1·710	78	63·67	1·2066	28	22·85
1·698	77	62·85	1·198	27	22·03
1·686	76	62·04	1·190	26	21·22
1·675	75	61·22	1·182	25	20·40
1·663	74	60·40	1·174	24	19·58
1·651	73	59·59	1·167	23	18·77
1·639	72	58·77	1·159	22	17·95
1·627	71	57·95	1·1516	21	17·14
1·615	70	57·14	1·144	20	16·32
1·604	69	56·32	1·136	19	15·51
1·592	68	55·59	1·129	18	14·69
1·580	67	54·69	1·121	17	13·87
1·578	66	53·87	1·1136	16	13·06
1·557	65	53·05	1·106	15	12·24
1·545	64	52·24	1·0938	14	11·42
1·534	63	51·42	1·091	13	10·61
1·523	62	50·61	1·083	12	9·79
1·512	61	49·79	1·0756	11	8·98
1·501	60	48·98	1·068	10	8·16
1·490	59	48·16	1·061	9	7·34
1·480	58	47·34	1·0536	8	6·53
1·469	57	46·53	1·0464	7	5·71
1·4586	56	45·71	1·039	6	4·89
1·448	55	44·89	1·032	5	4·08
1·438	54	44·07	1·0256	4	3·26
1·428	53	43·26	1·019	3	2·445
1·418	52	42·45	1·013	2	1·63
1·408	51	41·63	1·0064	1	0·816

The following table shows, in degrees Baumé, the proportion per cent. of sulphuric acid and of sulphuric anhydride in sulphuric acid of different densities at a temperature of 15°.

Degrees Baumé	H_2SO_4 per cent.	SO_3 per cent.	Degrees Baumé	H_2SO_4 per cent.	SO_3 per cent.
5	5·4	4·3	49	61·1	50·0
10	10·9	8·9	50	62·6	51·1
15	16·3	13·3	51	63·9	52·2
20	22·4	18·3	52	65·4	53·4
25	28·3	23·1	53	66·9	54·6
30	34·8	28·4	54	68·4	55·8
33	38·9	31·8	55	70·0	57·1
35	41·6	34·0	56	71·6	58·4
36	43·0	35·1	57	73·2	59·7
37	44·3	36·2	58	74·7	61·0
38	45·5	37·2	59	76·3	62·3
39	46·9	38·3	60	78·0	63·6
40	48·4	39·5	61	79·8	65·1
41	49·9	40·7	62	81·7	66·7
42	51·2	41 8	63	83·9	68·5
43	52·5	42·9	64	86·3	70·4
44	54·0	44·1	65	89·5	73·0
45	55·4	45·2	65·5	91·8	74·9
46	56·9	46·4	65·8	94·5	77·1
47	58·2	47·5	66	100·0	81·6
48	59·6	48·7			

One of the most important properties of sulphuric acid is its solvent action. It dissolves nearly all metals, either when diluted or in the concentrated state; in the former case with development of hydrogen gas, in the latter under reduction to sulphurous acid. Thus, the metals iron, zinc, cadmium, etc., dissolve in diluted sulphuric acid with evolution of hydrogen; the metals mercury, copper, silver, etc. dissolve in concentrated sulphuric acid with evolution of sulphurous acid. The chemical change in the first case is represented by the equation:

$$\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 + Zn = \left.\begin{matrix}SO_2\\Zn\end{matrix}\right\}O_2 + H_2.$$

that in the second case by the equation:

$$2\left(\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2\right) + Cu = \left.\begin{matrix}SO_2\\Cu\end{matrix}\right\}O_2 + SO_2 + 2\left.\begin{matrix}H\\H\end{matrix}\right\}O.$$

Other reducing agents, such as carbon, sulphur, phosphorus, etc., also exert a deoxidising action upon concentrated sulphuric acid, like the metals; but a higher temperature is necessary.

Sulphuric acid combines very energetically with free bases forming sulphates, and it is only by a few other acids, and in a few instances, that it can be separated from such compounds without the aid of heat.

Nordhausen oil of vitriol, or fuming sulphuric acid, must be considered as a mixture of variable quantities of sulphuric anhydride and sulphuric acid monohydrate. Its preparation and properties have been known longer than the ordinary acid.

Preparation.—Sulphuric acid is formed by the hydration of sulphuric oxide, also by the oxidation of sulphurous oxide, and by the action of concentrated nitric acid or of aqua regia upon sulphur, but these processes are seldom had recourse to except for special purposes. In the preparation of sulphuric acid on a large scale, sulphurous oxide produced by burning sulphur or pyrites is converted into sulphuric acid by means of some powerful oxidising agent. Although sulphurous oxide in aqueous solution is gradually oxidised to sulphuric acid by exposure to the air, this change does not admit of practical application when large quantities of acid are required.

The oxidising agent now universally employed for oxidising sulphurous oxide to sulphuric acid is nitric acid. The greater part of the oxygen, however, is not derived from the nitric acid, but is obtained indirectly from the air as the result of a complex chemical process that takes place in the lead chambers used for the purpose. The presence of water is very important, as will be seen presently.

Manufacture of Fuming Oil of Vitriol.—A comparatively small quantity of sulphuric acid is made in Saxony and Bohemia by distillation from calcined ferrous sulphate or 'green vitriol,' also recently from acid sodium sulphate.

Preparation from Vitriol.—The method of procedure in Bohemia is the following. Pyrites, freed by elutriation from admixtures of clay, is heated to redness in fire clay retorts, out of contact with air, according to the method described on page 99, and the sulphur distilling off, amounting generally to 14 or 15 per cent., is collected. The residue left in the retorts is ferrous sulphide, which is allowed to disintegrate and oxidise in the air, a process which requires several years. The oxidised product is lixiviated and the lye evaporated to crystallisation by the heat of the retort furnaces. The first crystallisation yields tolerably pure ferrous sulphate (green vitriol). The mother liquor is evaporated to dryness, and the residue calcined so as to convert the ferrous sulphate into basic ferric sulphate. This conversion is, however, never entirely accomplished, the calcined material always containing small quantities of ferrous sulphate, and with this some water which is given off in the process of heating to redness. The ferrous sulphate also decomposes with formation of sulphuric anhydride and sulphurous oxide, according to the equation:

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$

The basic and neutral ferric sulphates, when heated to redness, yield ferric oxide and sulphuric oxide or anhydride. The small quantity of water contained in every sample of Nordhausen oil of vitriol is derived from the water contained in the ferrous sulphate, and given off when the calcined vitriol is heated to redness.

The distillation of fuming sulphuric acid from calcined vitriol is carried out in a kind of galley furnace, both sides of which are fitted with a double row of retorts, 34 in number, lying over each other, and above these often a third row of 32 retorts. The retorts (B B) are made of fire clay, and have a bore of about 8 inches and a length of 32 inches. Each retort is furnished with a receiver (A), of the same size and form as

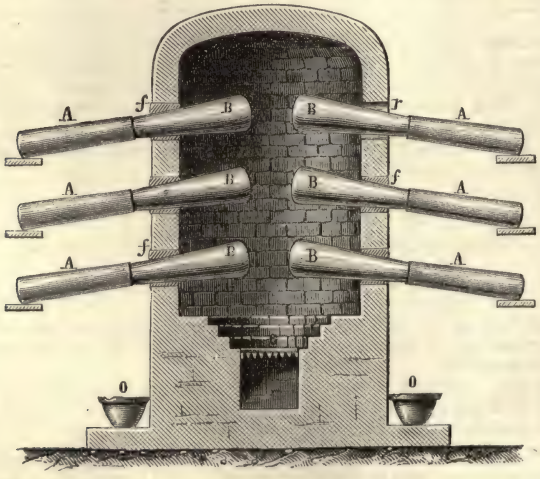


Fig. 47.

itself. The 200 retorts hold 5 cwts. of calcined vitriol, and are so heated (2 tons of brown coal being used) as to yield 2 cwts. of acid and 2½ cwts. of residue (colcothar or ferric oxide). At the beginning of the process only water escapes, then sulphurous oxide and oxygen, and finally sulphuric anhydride and hydrated sulphuric acid distil over, which mix and condense in the receivers.

Since the manufacture of fuming sulphuric acid in the above way involves considerable loss of sulphuric acid, which escapes as sulphurous oxide and oxygen, it has of late been the custom to prepare Nordhausen oil of vitriol from ferric sulphate; the latter being obtained by the treatment of colcothar with ordinary sulphuric acid, and evaporating the product to dryness. On distilling this ferric sulphate, sulphuric anhydride of great purity is obtained and a small quantity of ordinary sulphuric acid is placed in the receivers, with which the anhydride readily mixes. The residue in the retorts is used again for the preparation of ferric sulphate.

Fuming Sulphuric Acid from Sodium Bisulphate.—This method of preparing fuming sulphuric acid, which has recently been much adopted in France, is analogous to that above described. Retorts of a similar kind are used, in which the sodium bisulphate is heated until sulphuric anhydride begins to distil over, when glass receivers are attached to the necks of the retorts.

Fuming sulphuric acid is further manufactured by heating to redness dried Glauber's salt with boracic acid, and condensing the vapour in receivers containing ordinary sulphuric acid. The residue in the retorts is employed in the preparation of borax.

Manufacture of Sulphuric Acid in Lead Chambers.—The preparation of this acid on a large scale in leaden chambers dates from the year 1746, when Dr. Roebuck, of Birmingham, erected the first leaden chamber at Prestonpans, near Edinburgh.

The formation of sulphuric acid from sulphurous oxide by the agency of nitric acid and the lower oxides of nitrogen depends upon a number of consecutive chemical changes. Till recently the following three changes were supposed to take place:

1. Conversion of sulphurous oxide and concentrated nitric acid into sulphuric acid and nitrogen peroxide according to the equation:

$$SO_2 + 2\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O = \left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 + 2NO_2.$$

2. Reproduction of nitric acid from a portion of the nitrogen peroxide by the action of water; another portion of it becoming reduced to nitric oxide, according to the equation:

$$3NO_2 + \left.\begin{matrix}H\\H\end{matrix}\right\}O = 2\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O + NO.$$

3. The nitric oxide formed in the second process combines with oxygen from atmospheric air admitted into the chamber, and is thus converted into nitrogen peroxide, according to the equation:

$$NO + O = NO_2.$$

This nitrogen peroxide is again decomposed by the action of water producing a further quantity of nitric acid. According to the changes thus given the nitric acid originally employed is first of all deoxidised, and then by means of two consecutive chemical changes the products of the deoxidation are again converted into nitric acid: theoretically, therefore, it would appear from this that a small quantity of nitric acid should be capable of converting unlimited quantities of sulphurous oxide into sulphuric acid. But in the manufacture of sulphuric acid it is necessary to keep up a continual supply of nitric acid to the lead chambers, because the nitrogen introduced into the chambers in the form of atmospheric air, and escaping, after the oxygen associated with it has been absorbed, carries with it various oxides of nitrogen.

According to this view, it is nitrogen peroxide that effects the transfer of oxygen from the air to the sulphurous oxide by a constantly recurring conversion into nitric acid. Weber has suggested another view of the change, according to which it is not nitrogen peroxide, but nitrous anhydride which performs the important function of transferring oxygen from atmospheric air to the sulphurous oxide in the lead chambers. He assumes the following consecutive changes to take place:

1. By the contact of sulphurous oxide with a dilute mixture of sulphuric acid and nitric acid, such as is found in the lead chamber, it is oxidised to sulphuric acid, the nitric acid being reduced to nitrous anhydride, according to the equation:

$$2SO_2 + 2\left(\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O\right) + H_2O = 2\left(\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2\right) + N_2O_3.$$

2. The nitrous anhydride in the first instance dissolves in the sulphuric acid. By the reaction of nitrous anhydride thus formed with further portions of sulphurous oxide, it is reduced to nitric oxide, while the sulphurous acid is oxidised to sulphuric acid according to the equation:

$$SO_2 + N_2O_3 + H_2O = \left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 + 2NO.$$

3. Conversion of the nitric oxide into nitrous anhydride by contact with atmospheric air according to the equation $2NO + O = N_2O_3$. In this way the substance is reproduced which acts upon sulphurous oxide in the manner above described.

The important fact that, in the lead chambers, nitric oxide gas is oxidised to nitrous anhydride, and not to nitrogen peroxide, has been confirmed by Winkler, who has proved that in presence of sulphuric acid, nitric oxide is never oxidised to nitrogen peroxide, but always to nitrous anhydride.

Accordingly, nitrous anhydride, and not nitrogen peroxide, must be considered as the medium by which oxygen is transferred from atmospheric air to sulphurous oxide in the manufacture of sulphuric acid.

An apparatus for the preparation of sulphuric acid is represented in section by figs. 48 and 49. A is the furnace in which the sulphur is burnt, the hearth consisting of a

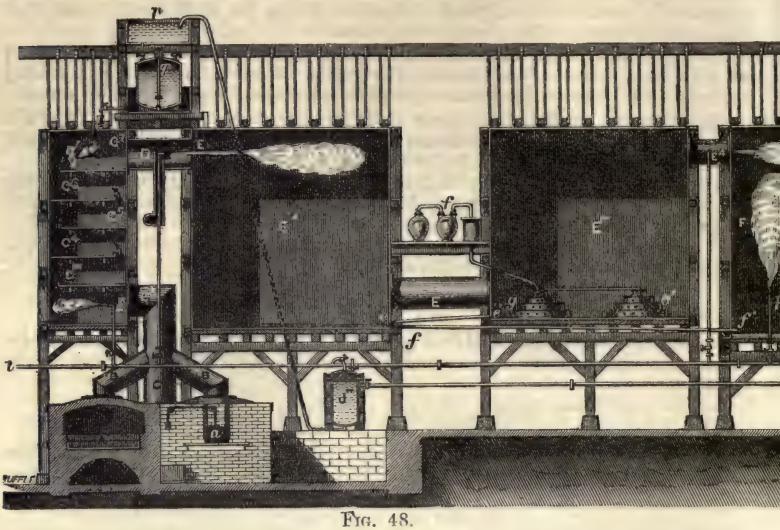


FIG. 48.

plate of cast or sheet iron, with the edges turned up from 3 to 4 inches high. A steam boiler is often fitted above this furnace, so as to be heated by the burning sulphur, and furnish the steam required in the chamber. The more general plan, however, is to have at least an additional boiler ready to do duty in case of repairs. The acid vapour of the chambers is prevented from getting into the boiler by a valve, which is opened by the steam escaping from the boiler, but prevents the access of gas from the chambers. The figure represents two furnaces for the production of sulphurous acid; one shown in section (A), the other in elevation with a sliding door (*a*). The gas from these furnaces, consisting of sulphurous acid and air, escapes through the tubes (B B) and (C C′) into a small lead chamber (c′ c⁷), and from thence into the first lead chamber (E′). The tubes (C C′) and (D) have a sectional area double that of the tubes (B B), since they have to convey the entire quantity of gas passing through B and B. The tube (C) is sufficiently high to cause a draught, by which the gas is drawn forward from the sulphur burner. The draught is further increased by passing a jet of steam in the direction of D into the chamber (E′) and another through a pipe (C″) into the chamber (C″ c⁷). The gas passes from the first chamber (E′) through the pipe (E″) into the second chamber (E‴), where stoneware dishes (*g g′*) are placed terrace-like above one another, into which nitric acid is supplied from vessels (*f*) outside the chamber, and overflows from them so as to offer an extended surface to the gas in the chamber. The supply of nitric acid is either continual or intermittent. In the latter case an apparatus is placed between the acid holders and the chambers, which allows about 11 lbs. of nitric acid to flow into the chamber every half hour, or whatever quantity may be required. This apparatus consists of a vessel into which nitric acid is permitted to flow, and from which it cannot escape until the acid has reached the level of the discharge aperture. The discharge is regulated by a syphon arrangement, so that when it has once begun it does not cease until the vessel is emptied. Although nitric acid is constantly dropping into this vessel, the discharge is interrupted while it is being filled, because the syphon is then filled with air.

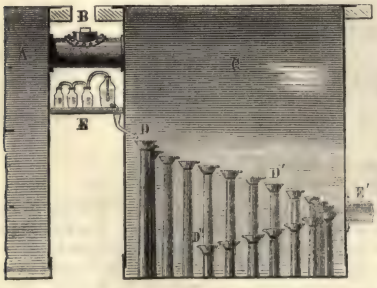


FIG. 50.

Instead of introducing the nitric acid into the chamber by means of the dishes just described, the arrangement represented by fig. 50 is sometimes employed. It consists

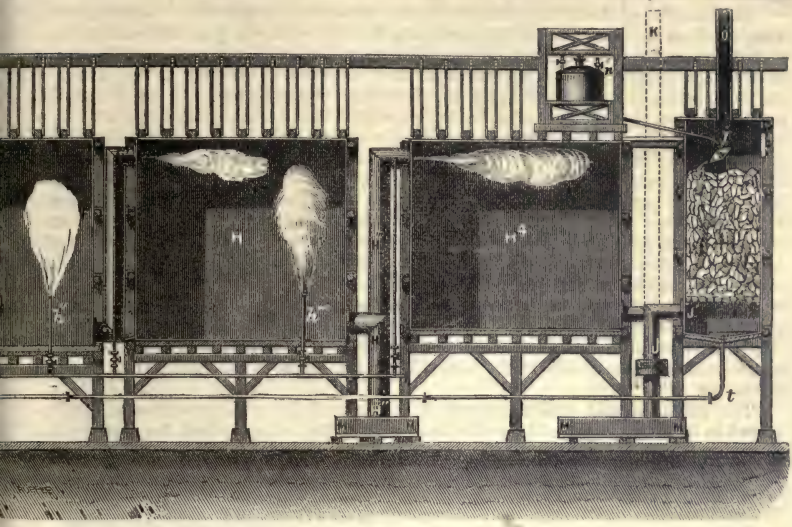


FIG. 49.

of a number of vertical tubes of stoneware having a funnel-shaped mouth provided with a lip. These tubes are arranged like the pipes of an organ, along the sides of the second chamber. The nitric acid is supplied from vessels outside the chamber into the tallest of these tubes, and when that is full it flows into the next, and so on, until it reaches the lowest (D″). In its long passage from the first to the last of the tubes, the nitric acid exposes a considerable surface to the surrounding vapours of sulphurous acid, air, and steam, and is to a great extent reduced to nitric oxide.

Since the sulphuric acid formed in this chamber contains much nitric acid and other oxides of nitrogen, it is conducted back, through a pipe (*e′e*, fig. 48) into the first chamber (E′), the floor of which is somewhat lower. Here it is exposed to a fresh mixture of gases containing a large amount of sulphurous acid which reduces the nitric acid contained in it. From this chamber the sulphuric acid is conducted through a tube (*ff″*) into the third chamber (F), where the whole of the acid produced by the series of chambers eventually collects, and from whence it is drawn off at intervals or in a continuous stream. The floor of this chamber is therefore lower than that of the other chambers. The gas escaping from the chamber (E‴) also passes through the tube (E⁴) into the larger chamber (F), only the ends of which are shown in figs. 48 and 49. In order to increase the draught necessary for the complete mixing and decomposition of the gas, a jet of steam is passed into F, in the same direction as the gas travels; while at the bottom of the chamber there are several tubes (*h h″*), which supply the steam required for the production of sulphuric acid. The most judicious arrangement of these steam tubes is to fit them in at the sides or roof of the chambers, so as to avoid joints at the bottom. The gas that is not condensed in this chamber passes through a tube (G G″) into a fourth chamber (H), into which steam is passed as before, both in the direction of the gases, and also through a tube (*h‴*) fitted in either the side, top, or bottom of the chamber. The gas then passes through the tube (H′ H″) into a closed reservoir (M M), furnished with partitions, in which it circulates before passing through the tube (H‴) into the fifth chamber (H⁴). Steam is passed into this chamber to force the gas into a second reservoir (M′ M″) similar to the last, and then it either escapes through the tube (J K) direct into the atmosphere, or through (J J′) into an apparatus, where the remaining portion of nitrous gas is condensed. The tube conducting the gas into the air or into the condenser is furnished at (J) with an arrangement for regulating the rate at which the gas passes. This is effected by means of a horizontal partition fitted into the box, and perforated with round holes an inch wide, the joint area of which exactly corresponds to the sectional area of the tube. The rate of passage of the gas is regulated by closing these holes with

leaden plugs, the regulator for this purpose being furnished with a wooden door covered with lead.

Condensation of the Nitrous Gas (containing nitrogen peroxide and nitrous anhydride), escaping from the Chamber.—The gas escaping from the chimney (IK) still contains considerable quantities of nitrogen oxides, which would be lost if not condensed by means of a special apparatus. An apparatus for this purpose was invented by Gay-Lussac; its construction is represented in fig. 49. It consists of a cylinder (J′j), into which the gas passes from the tube (J J′) after having circulated through the reservoir (M′M″). This cylinder has a perforated bottom supporting a column of pieces of coke. Sulphuric acid of sp. gr. 1·690 to 1·727 is allowed to trickle slowly from the reservoir (N) over the coke, its equal dispersion being secured by means of a cup (*l*), divided into two parts by a partition parallel to its axis, and turning on an axis on which it oscillates between two cross-bars. When one division is filled with sulphuric acid, it topples over and empties itself, and the acid flows into the other division, and so on. The sulphuric acid flowing down over the coke meets the ascending chamber gas, and absorbs the nitrogen peroxide and nitrous anhydride, and the gas, which then contains only very slight traces of nitrous gases, escapes through the chimney (o). The amount of nitrous gases absorbed amounts to 3½ per cent. Since the absorption of the nitrous gases is more complete in proportion to the dryness of the gas, it is passed through a layer of concentrated sulphuric acid in the reservoir (M′ M′), before it enters the Gay-Lussac's condenser.

The sulphuric acid which collects on the floor of the cylinder, and contains dissolved in it nitrogen peroxide and nitrous anhydride, is conducted for further use through a long tube into the reservoir (J″), and is pumped from thence into another reservoir (*p*). From *p* this acid flows into the vessel (*q*), and from thence through a funnel and a swinging cup similar to the one marked *l* into the anterior chamber (c'', c^7). The acid trickles down over the shelves (c^6, c^5, c^4, c''') to the floor of this chamber, finding its way eventually into the first leaden chamber (E′). The shelves (c^6, c^5, c^4, c''') serve to present a large surface of the acid to the joint action of the sulphurous acid and air passing into the anterior chamber (c'', c^7), through the tube c c′, and the steam let in at c''. The nitrous gases contained in the sulphuric acid are thereby reduced and the sulphurous acid oxidised to sulphuric acid. By the use of this apparatus oxides of nitrogen are again rendered serviceable, which would otherwise be lost, and be injurious to the neighbourhood surrounding the manufactory.

MODIFICATIONS IN THE APPARATUS, ETC.—Since the introduction of the manufacture of sulphuric acid on a large scale, many improvements have been made in the details of the chamber system, the most important of which are the following:

The Sulphur-Burner or Furnace.—These furnaces have various forms and arrangements. In their construction it must be remembered that the combustion of 100 pounds of sulphur per day of 24 hours requires a burning area of about 5 square feet. Consequently, the number of such burners depends upon the extent of the manufacture. In many works four or six sulphur furnaces are employed, their gaseous products passing into the chambers through a common tube.

Since it is important that the combustion of the sulphur should admit of being regulated, so as to avoid the too rapid supply of sulphurous oxide to the chambers, and to prevent its entering too hot, some sulphur burners are furnished with an arrangement for admitting cold air beneath the iron plate upon which the sulphur is burnt. The grating admitting air into the furnace for the combustion of the sulphur is furnished with a register for regulating the draught.

In some works, for instance one at Corbetha, near Weissenfels in Prussia, the gas from the burners is passed through a long brick flue furnished with partitions, in order to cool it sufficiently before passing into the lead chambers. In Kuhlmann's works, the sulphur is burnt in cast-iron retorts having a hemispherical cross section. Each furnace holds four such retorts, the retorts having a door in front for charging with sulphur, and regulating the draught, the gas escaping from an opening at the other extremity and passing through long tubes into a suitable cooling chamber. In other works the sulphur burners, instead of being surrounded with brickwork, are fitted on one or two sides with cast-iron plates which serve to cool the gases to a considerable extent.

Very well worth notice are the so-called continuous burners, in which a constant and uniform combustion of sulphur to sulphurous oxide is effected.

In a burner of this kind invented by Petrie, a cast-iron plate with the rim bent upwards is supported on brickwork, and forms the floor of the burner. Openings are left in the brickwork basement, so that when necessary air can circulate under the iron plate to cool it. The cover of the burner consists of an iron plate, also with a rim bent upwards, into which water is poured to cool the gases. The burner has a

door in front for admitting the air necessary for combustion and for the removal of the burnt residues. Opposite the cast-iron plate which forms the hearth of the burner is a grate forming with the hearth an angle of about 45°, upon which the sulphur to be burnt is placed. This grate is heated by the combustion of the sulphur in the burner, causing the sulphur laid on it to melt and trickle down upon the iron plate below, where, coming into contact with atmospheric air from the door in front of the furnace, it is burnt, and by its combustion generates heat enough to melt a fresh portion of the sulphur in the grate above, so that in this way a continual supply and combustion of sulphur takes place. The gaseous product of combustion escapes into a long brickwork flue, where it is cooled before passing into the lead chambers. In order to prevent the grating from being too strongly heated and the sulphur from melting too rapidly, a screen of sheet iron is placed parallel to the iron hearth between it and the grate. Up to the present time it has not been found possible to construct the burners so as to insure a perfectly equal flow of sulphur.

Blair has constructed an apparatus depending upon other principles. The action of his burner depends upon the sulphur being vaporised in a separate chamber, and then burnt in another chamber, the sulphurous oxide and air being then passed into a chamber immediately above the combustion furnace, in which the nitrous vapours are evolved, the mixture of nitre and sulphuric acid being charged into this chamber from the side, either in pots or small trucks. The quantity of air admitted into the chamber where the sulphur is vaporised is just sufficient to produce, by combining with some of the sulphur, heat enough to vaporise the remainder.

Production of Sulphurous Oxide.—The use of sulphur for this purpose has been largely superseded by the production of sulphurous oxide by roasting native metallic sulphides, which now constitute the chief source of the sulphur used in the manufacture of sulphuric acid. (See *ante*, p. 107.)

Among the different native metallic sulphides, iron pyrites is so abundant that it is largely employed in the manufacture of sulphuric acid. Copper pyrites, or at least pyrites containing copper, is also roasted for the preparation of sulphuric acid as well as blende.

Assuming that pyrites contains on the average 47 per cent. of sulphur, this would represent from 40 to 42 per cent. of sulphur available in the manufacture of sulphuric acid.

The amount of sulphur in pyrites varies somewhat considerably according to the locality from which it is obtained. Pure iron pyrites contains 53·33 per cent. of sulphur, but it is never found of such purity in great quantities. Besides this, the admixtures occurring in pyrites which lessen its amount of sulphur may sometimes have a directly injurious effect. Among these are the compounds of arsenic which pass over into the sulphuric acid itself, and lead compounds which retain the sulphuric acid, etc.

A further point of importance in the use of pyrites is the nature of the burnt pyrites. In many cases this is not further worked, but it often happens when copper pyrites is used that the roasted material may be profitably worked for copper. Some sulphuric acid works indeed are supplied with pyrites almost gratis by the proprietors of copper works in exchange for the burnt pyrites. The burnt pyrites is also often worked for green vitriol and for Nordhausen sulphuric acid.

The use of pyrites as compared with sulphur has, however, many decided disadvantages which must be taken into consideration. The acid obtained from pyrites is not so pure, generally containing much arsenic; the loss of chamber gas is greater, owing to the larger quantities of air employed; more especially is the consumption of nitric acid greater, being nearly 50 per cent. more than that required when pure sulphur is burnt. The process is more difficult to regulate; the pipes or tubes conducting the gas from the furnaces to the lead chambers must be of greater length, on account of the high temperature required for roasting the pyrites. Another point of very great importance in the use of pyrites is that the leaden chambers last on an average little over a third as long as they do when sulphur is used.

As already mentioned, pyrites varies in value according to locality. The chief pyrites deposits are the following: Spain; from Tharsis, province Huelva and Sierra. The pyrites found here contains from 46–50 per cent. sulphur, and from 3–5 per cent. copper. Portugal: province Alemtejo. This pyrites has the same composition as that found at Huelva in Spain, and forms a continuation of that bed. France has large beds of pyrites in the Rhône and Gard departments. This pyrites is worked in France at Chessy, St. Fonds, St. Christ, Oseraie, Pontet, as well as at Chauny, Mühlhausen, Mannheim, Thann, Dieuze, Lille, Rouen, and Paris. It contains from 45–47 per cent. of sulphur, and yields from 120–126 per cent. of sulphuric acid of sp. gr. 1·767. The copper amounts to 3 or 4 per cent., and this metal is worked up on a large scale, especially at Chessy. The pyrites from Alais, departement du Gard, contains $\frac{1}{10000}$ part of gold. The Belgian pyrites from the provinces Namur and Liége contains from 47–49 per cent. sulphur, and also as a rule much arsenic. Pyrites is found at Charleroi

which does not contain more than traces of arsenic. Germany has large beds of pyrites at Meggen in Westphalia. The amount of sulphur in this is 45 or 46 per cent., and that of arsenic very small. Beds of pyrites are also found in Ireland, but the sulphur does not exceed 44 per cent., and is generally only 30 per cent. The amount of copper contained in the Irish pyrites varies between $\frac{1}{8}$ and $1\frac{1}{2}$ per cent. Norway possesses very large beds of pyrites, yielding as much as 44 per cent. of sulphur. Italy has also considerable pyritical beds. St. Domingo exports to this country copper pyrites containing from $3\frac{1}{2}$–4 per cent. of copper.

Pelouze determines the amount of sulphur in pyrites by melting it with potassium chlorate, sodium chloride, and an exactly weighed quantity of calcined soda, which is partly converted into sodium sulphate and the remainder is titrated with normal acid. Lunge oxidises with concentrated nitric acid; De Ricqlès with nitric acid and potassium chlorate, precipitating the sulphuric acid with barium chloride. According to Anthon the amount of pure pyrites in a sample of ore may be ascertained from its specific gravity.

Before pyrites is roasted it requires breaking up into equal pieces from 1 to $1\frac{1}{2}$ inches in diameter, so that the air penetrates a layer of such pieces 30 or 32 inches in depth.

Well-arranged roasting furnaces only require to be heated with coal or wood at the beginning of the operation, the heat necessary for the continuation of the process being furnished by the combustion of the pyrites itself. The construction of the roasting furnaces varies with their age, the kind of ore to be roasted, and the amount of heat required. Pyrites that has afterwards to be worked for copper is not roasted at so great a heat as that containing little or no copper.

Shaft Furnaces or Kilns.—Figs. 51 and 52 represent a very simple kind of furnace for roasting pyrites. This consists of the fire-place (A), with strong horizontal grate, surrounded by thick brickwork. In order to set the furnace going, it is heated to bright redness internally with fuel, and pieces of pyrites, in small quantities at a time, are then thrown in through the opening (*e*), fresh portions being added according to the rate of combustion at the surface, until the layer of pyrites is about 32 inches high. Air passes into the furnace through the opening A, fig. 52, its passage being regulated by the damper (B). The roasted pieces of pyrites are poked down with a rod thrust between the bars of the grate, whereby the circulation of air is assisted. At every fresh charging the lower opening is closed by letting down the damper B, so as to cause the draught to enter for a moment through *e*, and thereby protect the workman from the vapours. The gaseous product of combustion escapes through the tube *d*. A number of furnaces of the kind (A B C D E F, fig. 53) are built round a common chimney (*f*), through which the gas passes into the lead chambers. The chimney (*f*) must be also in communication with the air, so that the smoke from the fuel used at the beginning of the operation may escape.

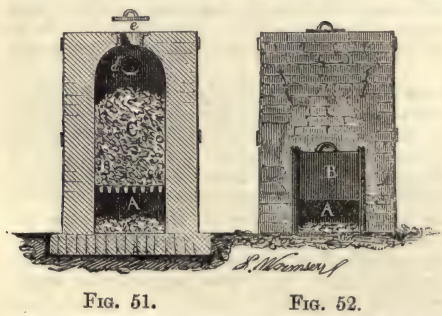


Fig. 51. Fig. 52.

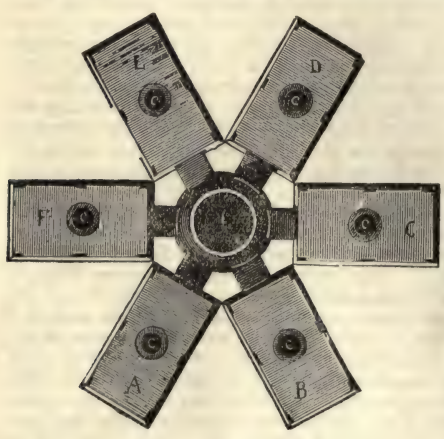


Fig. 53.

The arrangement shown by figs. 54, 55, and 56, used at Chessy, is of similar construction. A A are the pyrites furnaces, sixteen of which are arranged around a chimney (H). This chimney is formed of fire bricks below, and of a cast-iron tube (I, fig. 55), ending in a tube of sheet iron (J)

fitting into the lead chamber at K. The fire-place of each furnace is 5 feet long, 32 inches wide, and 40 inches high. Beneath are lateral openings (*b b*, fig. 56), each 8 inches

FIG. 54.

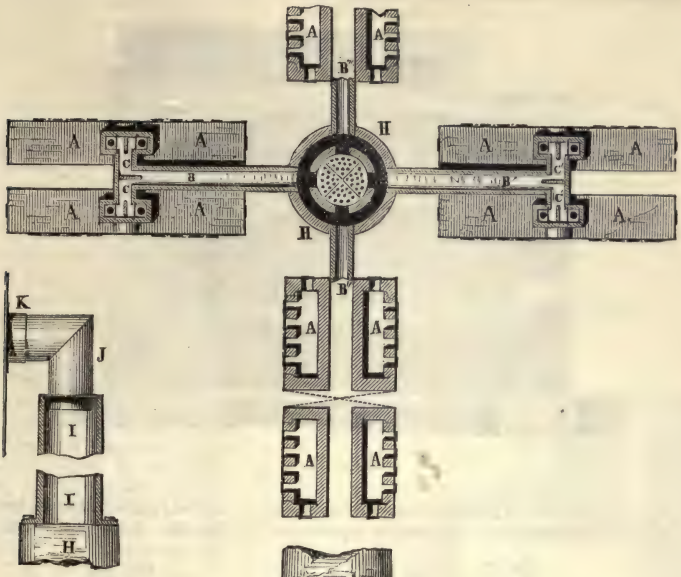


FIG. 55.

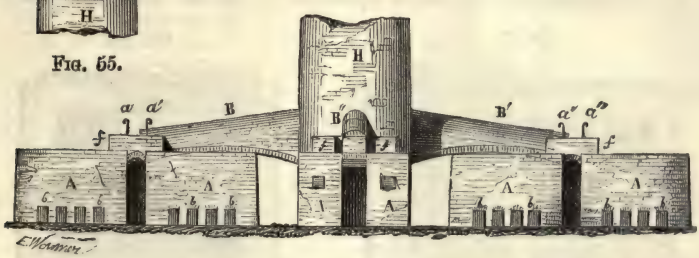


FIG. 56.

wide and 10 inches high, closed by doors of sheet or cast iron. Each of these doors has five round holes about ½ inch wide, for admitting air. An opening at the side, higher up, serves for admitting the charge of pyrites. Four furnaces of the kind are arranged together, and communicate with one another through horizontal flues (*c c*, fig. 54). The combustion gas passes from these flues through the tunnel (B', fig. 56) into the chimney (H). The dampers (*a a' a'' a'''*) are for the purpose of regulating the draught of each furnace. Above the opening of the side tunnels in the large chimney is a perforated fire-clay plate 4¾ inches thick, and covered with pieces of coke or bricks, serving to retain the smoke. When it is desired to set these pyrites furnaces going, the elbow (J, fig. 55) which connects the chimney with the lead chamber is removed, and each furnace is charged with a layer of burnt pyrites to a height of about 24 inches in such a manner that it sinks towards the discharge aperture. The next thing to be done is to throw in dry fuel, to heat the furnace to bright redness, to remove the still glowing coals, and to charge them with about 1 cwt. of pyrites. When the furnaces have been thus set in operation, the elbow (J) is again fitted on, and luted, and fresh charges of 1 cwt. at a time are added at intervals of three hours. At intervals of twelve hours the roasted product is removed through the openings *b b*. Should the temperature of any one of the furnaces rise too high, the roasted product is removed after eight hours, and by opening one of the doors (*b b*) the temperature is lowered to a red glow, so as to prevent the pyrites from fusing.

After the heating of the sixteen furnaces the pyrites burns without any fuel. This

furnace arrangement of sixteen furnaces admits of the roasting of $6\frac{1}{4}$ tons of pyrites every 24 hours, and assuming that to contain 40 per cent. of available sulphur, it corresponds with $7\frac{1}{2}$ tons of sulphuric acid.

Freiberg Pyrites Burner.—This has a form something like a blast furnace; the hearth is arched like a saddle and inclines towards the discharge aperture.

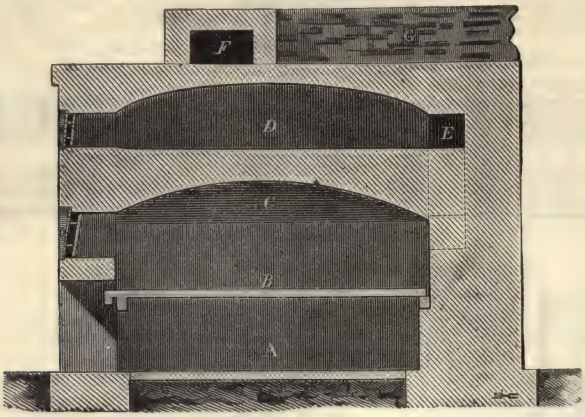


Fig. 57.

Hearth Furnaces.—In a few works where easily combustible pyrites is used, burners are employed having the construction represented by fig. 57. After the brickwork has been brought to a red heat, the pyrites is thrown upon the grate (B) in a layer thick enough to effect the continuation of the combustion without the further use of fuel. The calcined product falls through the bars of the grate into the ash-pit (A). The gaseous products of combustion, consisting of sulphurous oxide, nitrogen, air, etc. escape over a brickwork partition into a chamber (C), where a number of cast-iron pots charged with nitre and sulphuric acid are placed, in order to be heated by the hot gas. Instead of pots, pans of cast iron are sometimes employed. The nitrous vapours thereby evolved mix with the other gas, which passes through a brick-work flue, indicated in the figure by dotted lines, and through E into a reverberatory

Fig. 58.

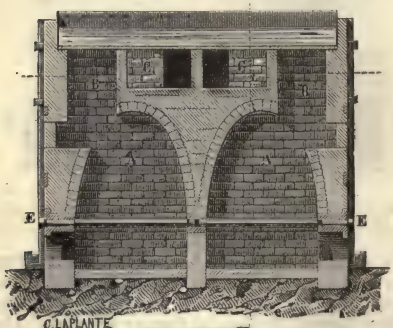
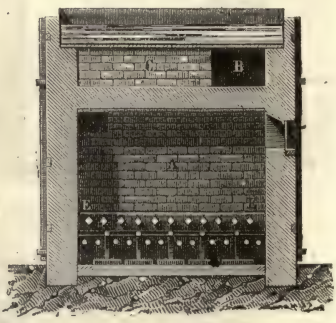


Fig. 59.



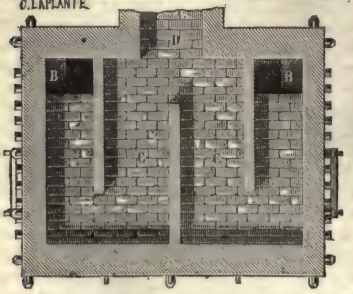
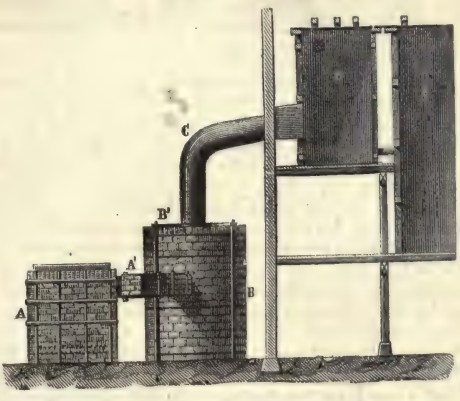


Fig. 60.

furnace (D), where ore dust can be roasted. From thence the gas escapes through the horizontal flue into the chief chimney, and finally into the lead chambers.

Many improvements have recently been made in pyrites furnaces, with the object of effecting more perfect calcination of the pyrites and greater economy of heat. Figs. 58, 59, and 60 represent a pyrites furnace employed at the same time for concentrating the chamber acid to sp. gr. 1·65. AA are a couple of calcining furnaces, the arrangement of the grate of which presents characteristic features. This grate consists of square iron bars, the sides of which are each $1\frac{5}{8}$ inches wide. The ends of these bars are rounded, and they lie in ring-shaped iron frames, in which they can be turned by means of a key. When the bars lie so that two of the sides are vertical and two horizontal, and the corresponding sides of all the bars are parallel, the distance between each pair of bars is $1\frac{1}{4}$ inches, sufficient to allow the roasted pieces to pass down between the bars into the ash pit; but when all the bars are turned 45°, the distance between each pair is not more than half an inch; and this lessens the draught. The grates have each a length of $6\frac{1}{4}$ feet and a width of $3\frac{3}{4}$ feet. The entire charge of the furnace amounts to 8 cwt. of pyrites, eight charges being thrown in in the course of 24 hours, in charges of 1 cwt. at a time and at intervals of 3 hours between each charge. The pyrites is thrown in through the doors, at the upper part of the arch of each furnace; the calcined residues being drawn out through the doors of the ash-pit. The doors of the ash-pits are furnished with holes $1\frac{1}{4}$ inches in diameter, through which air passes under the grate, the draught being regulated by opening or closing the holes. The entire charge remains in the furnace $2\frac{1}{2}$ to 3 feet high for 48 hours. The gaseous products of combustion ascend in the flues (B), pass underneath an iron plate supporting a leaden pan, and escape through the flues (CC) into a horizontal flue (D).

Fig. 61.



Figs. 61 and 62 represent an entire system of pyrites burners of the above kind, connected with the lead chambers. AAA are the furnaces; AA', the horizontal furnace flues, supported by iron plates and rings; BB, a brickwork tower, where the gases combine and a quantity of flue-dust collects; C, an elbow of cast iron, fitted into a leaden flange, through which the gases are conducted into the first small lead chamber (D), which serves to condense arsenical vapour, at the same time the flue-dust, which contains selenium and thallium, is here deposited. From this chamber the gas passes into the second chamber (E, fig. 62), and comes into contact with nitric acid, trickling down in a series of cascades.

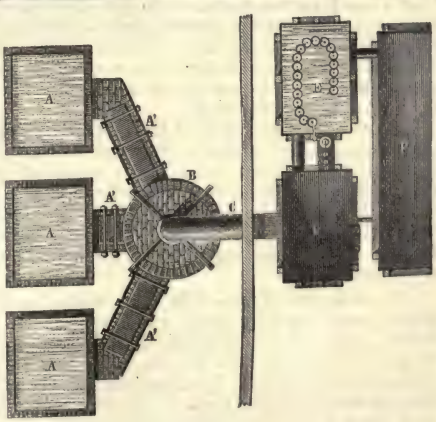


Fig. 62.

Calcination of Pyrites Dust. — Many propositions have been made with the view of utilising this material. In some places the dust is mixed with clay into round lumps, or bricks, dried and burnt in the ordinary pyrites furnaces. This plan has the disadvantage that the bricks or lumps are apt to crack and crumble when heated, thus stopping up the grate and preventing due circulation of air.

Figs. 63 and 64 represent a calcining furnace for ore dust constructed by Olivier and Peuret. The ore dust is spread upon six trays (c c′ c″ c‴ c⁴ c⁵), through the openings (*g g*), which are closed during the roasting, and is heated by the current of hot air and sulphurous acid passing up from the grate (B) of the furnace (A), where the pyrites is burnt. The gases escape through the uppermost division (D) and the flue (D′) into the chimney, from whence they are passed into the lead chambers. If at any

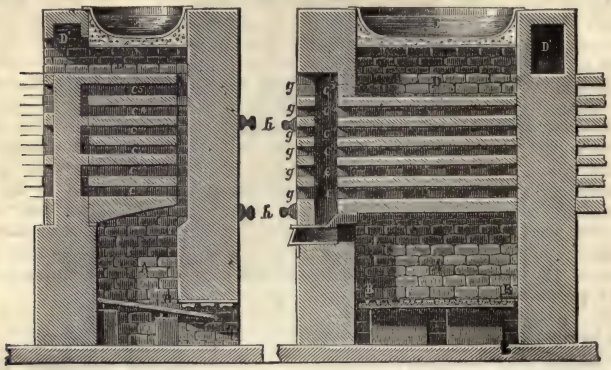


FIG. 63. FIG. 64.

period of the operation the roasting pyrites should have raised the temperature of the furnace too much, or have absorbed all the oxygen, air is admitted through an opening at the side on a level with the third tray. In proportion as the calcining progresses, the hard calcined mass is pushed with a bent rod inserted through G G into a vertical flue, and falls into a pit beneath the furnace, whence it is removed by a lateral aperture. This roasting apparatus is worked at Chessy, St. Bel, etc. A somewhat similar arrangement has been introduced by Mr. Hills for extracting sulphur from the ferric oxide that has been used for purifying coal gas.

In Spence's furnace the dust is strewn upon an inclined hearth of fire-clay slabs 80 to 100 feet long. The clay slabs are heated from beneath by direct fire, the calcination being effected by passing a current of air over the heated pyrites dust, which is spread upon the hearth at the end furthest from the fire in a layer two or three inches thick. After some time, when it has become hot, it is pushed forward towards the other extremity of the hearth and a fresh quantity is put in its place. This operation is repeated at intervals until the portion of pyrites first spread on the hearth has been transferred to the end where the fire is, and the whole of the hearth has been covered with a layer of pyrites. The length of time that must elapse before the ore is pushed forward must be determined for each kind of ore by experience, and it should be regulated so that by the time the ore reaches the further end of the hearth the sulphur should be completely burnt off. This roasting furnace is figured under the head of Copper Smelting.

In preparing many ores for the operation of smelting the removal of the sulphur they contain is very often a necessary preliminary, and in most instances the sulphur is not only wasted, but is likewise a source of great annoyance and injury to the neighbourhood. Therefore the adoption of some such method of roasting sulphuretted ores as that above described would be attended with considerable economy, inasmuch as the sulphurous oxide then produced could be converted into sulphuric acid. This furnace requires, however, too much air and fuel to render it practically useful and economical.

Gerstenhoefer's Kiln.—This kiln, which has been introduced of late into many places, serves also for roasting small ore, and is the best kind of kiln at present known. Fig. 65 represents this kiln in section along the line x z (fig. 66), and fig. 66 a section along the line v y (fig. 65); A A is the grate, about 15 feet wide, 7½ feet deep, and 40 feet high. The small ore brought in upon a special charging contrivance falls through the slit (D) upon the fire-clay bars (*m*), or ore distributors, and from these upon the first row of ore holders (*n*), from these on to the second, third, and following rows, until all the 15 rows have been passed, and it finally falls into a hollow, whence it is removed through a side opening at K. In order to set the oven going, a number of grate bars (*r*) are let in at *i*, and wood or other fuel admitted at *h* is then burnt upon the grate thus formed. The oven is thus made red hot, and when the ore begins to roast, it continues to do so without further application of heat.

When this has been done the grate bars (*r*) are removed and the necessary air admitted through the flue (*a*), the draught being regulated by a damper (*t*) in the arch (D). Opposite the upper surface of each row of ore bearers is a flue (*b b b*) leading outwards, and closed by an iron box (*c*); in the middle of each box is a hole closed by a clay plug, through which the state of the roasting charge may be observed. The gas passes from the upper part of the space (A) into the vertical flue (B), and from thence through *g* into the chambers (C and E) where the flue dust is deposited, and finally it is led into the vitriol chambers.

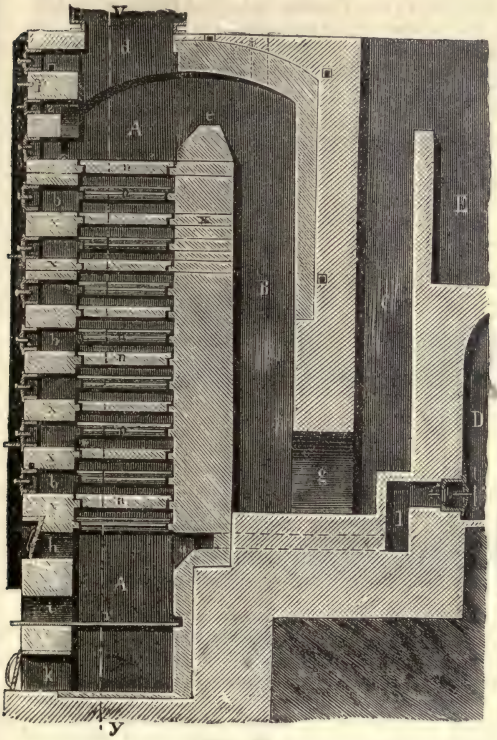


FIG. 65.

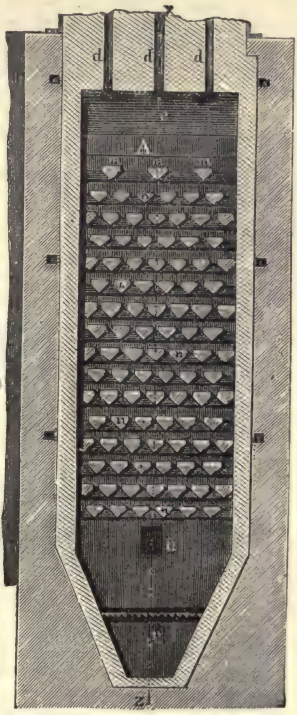


FIG. 66.

The further conversion of the sulphurous oxide into sulphuric acid is performed in the same way as when sulphur is used. The acid obtained is, however, generally contaminated with arsenic, from which it can be freed according to one of the methods described on page 134. Where acid is required absolutely free from arsenic, pyrites is not used, pyrites being only employed as a source of sulphuric acid when it is of no consequence whether the acid contains arsenic or not, as for instance in the preparation of superphosphates, or of sodium sulphate in the manufacture of soda, etc.

Since the pyrites used as a source of sulphur in the manufacture of sulphuric acid generally contains as much as 40 per cent. of iron, the residue left after the sulphur has been burnt off as sulphurous oxide would be worth working as an iron ore, and in some instances this has been done with some advantage. But besides iron, very many of the different kinds of pyrites worked in sulphuric acid factories contain copper, the amount varying from a mere fraction per cent. to 1·5 or 2 per cent. and upwards. The residue from the pyrites burners is therefore frequently as rich as some copper ores that are worked specially for the extraction of the metal, and on this account the extraction of copper has become an important feature of the operations carried on in works where sulphuric acid is manufactured upon a large scale from pyrites.

In this way, and by reason of the possible utilisation of the sulphurous oxide produced in roasting copper ores for the manufacture of sulphuric acid, copper smelting and the manufacture of soda, two branches of industry which were formerly quite

distinct, both as regards locality and the objects with which they were carried out, have come to be so intimately connected together that it seems a question whether the manufacture of sulphuric acid and soda in the districts of the Tyne, and parts of Lancashire, or the smelting of copper in South Wales, may not eventually be displaced and carried on concurrently. As it is, the extraction of copper from burnt pyrites is carried on to a considerable extent, either in alkali works or in their immediate proximity, and the methods by which this is done will be described in the section treating of Copper Smelting.

Methods of using the Nitrous Gases.—In many works, instead of liquid nitric acid, a mixture of nitre and sulphuric acid is used in the burners. For this purpose, cast-iron crucibles filled with equal parts by weight of nitre and sulphuric acid (specific gravity 1·551) are placed on the hearth of the sulphur burner. The crucibles are heated by the burning sulphur, and by decomposition of their contents, nitric acid, nitrogen peroxide, and nitrous anhydride are evolved, and pass along with the other gas into the lead chambers. According as Chili saltpetre or potassium nitrate are employed, sodium sulphate or potassium sulphate remains behind in the crucibles.

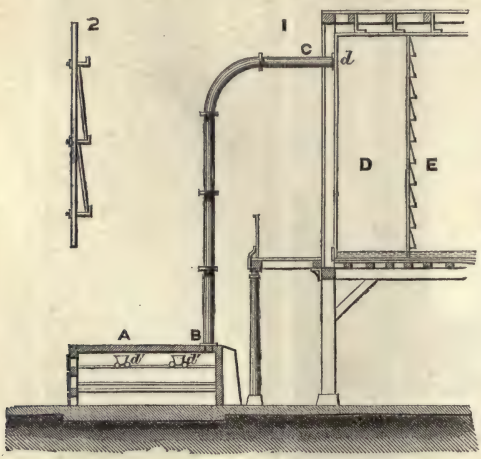


FIG. 67.

As soon as the decomposition is over, the crucibles are removed from the burner and replaced by others that have been fresh charged. The potassium or sodium sulphate is removed from the crucibles when cold, and admits of useful application.

The mixture of sodium or potassium nitrate and sulphuric acid is often brought into the burners in small trucks, which may be seen in the furnace (A), depicted in fig. 67. The trucks (*d'd'*) are made of cast iron and are run into the furnace on a small tramway set a little above the bed of the burner. Where trucks are employed, the burners are generally so constructed that the trucks may be run in at one end and out at the other.

The use of this mixture for the development of nitrous gases, instead of nitric acid itself, has some disadvantages, amongst the most important of which are, first, the fact that the vapour of nitric acid in the nascent state partly decomposes into nitrogen peroxide and oxygen, thus causing the transmission into the lead chambers of inactive oxide of nitrogen, and, secondly, the vapour, on account of the sulphuric acid it contains, attacks the tubes through which it passes much more energetically than the sulphurous oxide evolved by the simple combustion of sulphur.

Condensation of the Nitrous Gases.—Since the condensation of the nitrogen oxides, which escape from the lead chambers together with other gases, is a matter of great importance, inasmuch as the consumption of nitric acid may be thereby reduced to one-third, a number of contrivances have been proposed for effecting such absorption or condensation. The most important forms of apparatus that have been constructed for this purpose are the following.

The Gay-Lussac coke cylinder has been already described. It has received of late several improvements. For instance, there is placed between the swinging trough (*l*, fig. 49) and the coke layer, a lead plate, into which are fitted from 20 to 25 tubes of the same metal. When the sulphuric acid is tipped out of the trough into this plate, it flows through the tubes, and is thereby better dispersed over the coke than in the old arrangement. Further the perforated leaden floor of the cylinder for supporting the coke is now sometimes replaced by fire-bricks laid crossways over one another.

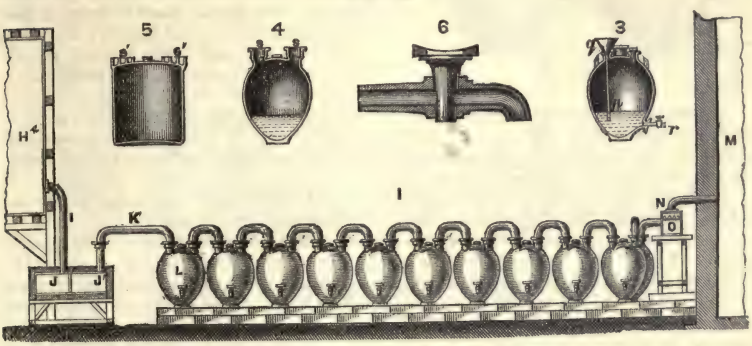
At some places, instead of the gases being passed through a reservoir with compartments (M'M', fig. 49), they are conducted through a long flue, from the other extremity of which a continual flow of sulphuric acid is kept up. By this means the gas is thoroughly dried, which is a matter of importance for the complete absorption. The pieces of coke in the Gay Lussac apparatus are replaced in some works by broken glass.

In Finkenhoher's apparatus the chamber gas passes into the bottom of a wide stoneware cylinder made of several pieces. Sulphuric acid flows down from above over alternating and inclined porous clay plates, and is drawn off below.

In all these forms of apparatus for the absorption of the nitrous gases, the chief thing is to secure an equally distributed flow of sulphuric acid from above. This is secured either by the use of Mariotti's vessel or by an ingeniously constructed balancing apparatus, which consists of a leaden vessel from which the sulphuric acid flows out below through a horizontal tube, terminating in a vertical cylinder. A leaden bucket floats upon the surface of the sulphuric acid in the cylinder attached to one of the arms of a lever, the other arm of the lever being in connection with a valve which opens and shuts the outlet of the leaden reservoir. Upon opening a cock at the lower part of the cylinder containing the leaden bucket the sulphuric acid flows out and consequently its level sinks, and the bucket sinks with it until it opens the valve of the reservoir and admits a fresh supply of sulphuric acid into the cylinder until the sulphuric acid in the cylinder has attained its former level. An apparatus of this kind when once properly set admits of a perfectly regular flow of sulphuric acid being obtained.

Condensation of Nitrous Gases in Absorption Bottles.—An apparatus of the kind is represented by figs. 68 and 69. The chamber gas passes from the last chamber

Fig. 68.



through the tube (F) into the vessel (J), and circulating from J to J′ is partly condensed. From J′ the gas passes through the tube (K) into the first carboy, thence into the second, third, etc., circulating through the three rows (L, L′, L″), and finally escaping into the chimney (M). A glass tube of the same width as the tube (K) is generally

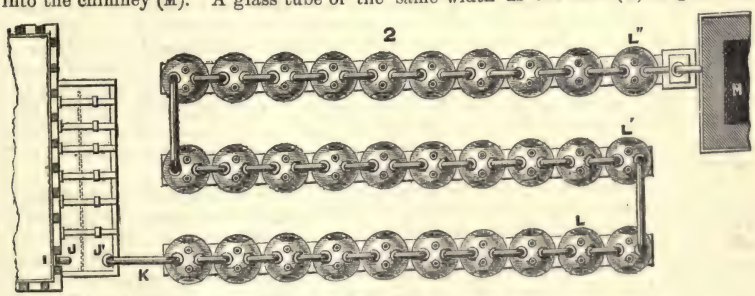


Fig. 69.

let into the latter for the purpose of watching the colour of the gases escaping from the chambers. Entire absence of colour or only very slight coloration indicates an insufficiency in the chambers either of nitrous gases or of steam. When the process is conducted properly the escaping gas is invariably of an orange colour.

The regulation of the draught in this apparatus is effected by causing the gas to pass through a box (O) provided with a perforated screen, the total number of apertures in which have together exactly the same area as the tubes through which the gas passes. The current is regulated by stopping up these apertures with inverted cups.

The carboys are filled to a certain height with sulphuric acid, having a strength of about 1·732. The carboys of the first row are emptied every day at intervals of an

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hour, their contents being run into the first chamber, and the carboys again charged with the acid from the second row of carboys; these again with the acid contents of the third row, and the latter are charged with fresh sulphuric acid of sp. gr. 1·732.

When the necessary contrivances are at hand the filling operation may be performed by a single workman. Since each carboy is emptied and recharged once daily, it follows that a given quantity of acid requires three days for its passage through the series before being run into the first chamber.

A carboy of the kind with funnel (*qp*) for filling, and cock (*r*) for running off the acid, is shown in section by **3**, fig. 68; **4** shows in section the tubulatures in which the connecting tubes are fastened; **5** shows the construction of a cylindrical carboy; and, finally, **6** shows the construction of the stone cock for running off the acid.

The emptying and refilling of the carboys is simplified by an arrangement represented by fig. 70. This consists of lateral tubulatures (*e e*), in which the level of the acid stands about an inch higher than the mouths of small glass siphons (*f f*). The latter when filled place the acid contents of the carboys in communication; for upon fresh acid being poured into the last carboy, this passes into the one next behind it, etc., until it finally reaches the first, becoming saturated with nitrous gases on its long journey. The gas is passed through the connecting tubes (C C) and (BB) in a direction contrary to the acid, thus coming on its way in contact with acid of continually increasing purity.

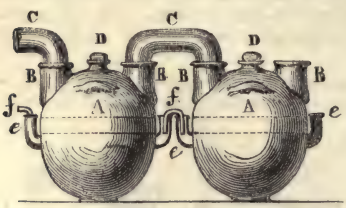


FIG. 70.

As regards the use of sulphuric acid for the absorption of nitrous vapour, experience has shown that the stronger it is, the more nitrous vapour is it capable of absorbing. Direct experiments made with sulphuric acid that had been treated with air and nitric oxide gave the following results:—

Sulphuric acid having a specific gravity of 1·711 absorbed 2·5 per cent. of nitrous anhydride, whilst that of specific gravity 1·846 absorbed 7·9 per cent.

According to the results of the above experiment, sulphuric acid having a specific gravity of 1·767 absorbs three times as much nitrous anhydride as acid of sp. gr. 1·711.

In some works the absorption of the nitrous vapour is effected by other substances than sulphuric acid; thus for instance milk of lime is sometimes employed, with which nitric oxide, nitrous anhydride, etc. combine, forming calcium nitrate. Further witherite (barium carbonate) in a state of fine powder and suspended in water is taken, for preparing by this means barium nitrate, and finally, in some cases, pure water is employed, which is allowed to trickle down through high towers something like the coke towers in the Gay Lussac apparatus.

Construction of the Chambers.—Propositions have often been made, but at present without success, to replace the lead used in making the chambers by a substance cheaper than lead. Thus amongst others the following substances have been proposed: zeiodolite, a compound consisting of sulphur and stoneware; panes of glass cemented together with a resinous cement; different kinds of stone plates joined together with a cement made of sulphur and sand, etc. Very well worth notice is the use of vulcanised caoutchouc or of gutta-percha, both of which substances have the advantage over lead of being cheaper and lighter than lead. On the other hand, they are more readily attacked by the chamber gas than lead is.

The number and size of the lead chambers, as already mentioned, are dependent upon the amount of sulphur that is to be burnt. The chief point in constructing chambers is to present as large a surface as possible to the chamber gases, so that they may mix intimately together and easily condense. For this reason it has recently been the practice to place a number of chambers one after another in a series, but it is possible to obtain the desired effect as well with two chambers as with six, provided contrivances are employed for increasing the surface. Fig. 67 represents an arrangement of this kind, in which the chamber is fitted with several partitions (B) made of iron rods extending from the floor of the chambers to the roof which they support. These rods are entirely covered with lead and are furnished with sheets of glass supported upon leaden hooks, as shown at **2**, fig. 67. These partitions are shorter than the width of the chambers, and are so placed alternately as to make the gas travel in a zigzag direction from one side to the other, increasing thereby the length of the passage and presenting to the gas a greater surface, by contact with which it is more easily intermixed and condensed. Chambers thus constructed have a more constant temperature than those which have only side walls.

In some works built upon this system, only one chamber is employed having a

capacity of 100,000 to 140,000 cubic feet. At the same time better results have been obtained in works where a second and smaller chamber with one or two curtains is attached to the large one. Of course, in chambers constructed on this system the acid collecting in the second chamber is made to flow back into the principal chamber, as in other cases.

Another plan may be here mentioned where only a single chamber is employed, but it is divided by curtains into three parts. These curtains are made of lead plates, reaching nearly but not quite to the bottom of the chamber, so that each division is separated from the other by the acid lying in the bottom of the chamber. The chamber gas is passed from one division into the other through tubes, the mouths of which are a little above the level of the acid in the chamber, while the other ends are inserted through the curtains at the upper part.

Arrangement of Chambers.—The general method of arranging vitriol chambers is that represented by figs. 48 and 49 where they are set one after another supported upon wooden frames. In this country, our temperate climate admits of the chambers being in the open air, but in France, Germany, and other parts of the continent they are generally roofed in and surrounded by light brickwork, on account of the more severe cold of winter.

The most convenient arrangement of the chambers is that in which the extremities are placed near each other, affording thereby a better opportunity of observing the process, inasmuch as these parts of the system are the most important and require the most attention. An arrangement of this kind is shown by fig. 71.

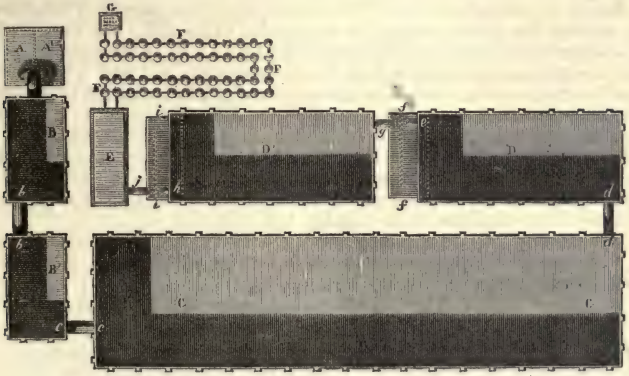


Fig. 71.

A A′ are burners, the plates of which are each 6½ feet long and 13 feet wide. A tube from 28 to 32 inches in width conducts the products of combustion, together with an excess of atmospheric air, into the small chamber (B), which is 23 feet in length, 13 feet wide, and 16¼ feet in height, and receives back from the second chamber the acid formed there, passing it on into the principal chamber. B′ is the second chamber, of the same dimensions as the first, with which it is in communication by means of the tube *b b*, which has a diameter of 24 to 27 inches. C C is the principal chamber, the floor of which is made lower than the floors of the other chambers, as it receives the condensed acid of the entire system. This principal chamber is about 120 feet long, 30 feet wide, and 20 feet high. D is the fourth chamber, having a length of 46 feet, a width of 20 feet, and is 16 feet high; it communicates with the principal chamber by the tube *d d*. *f f* is a refrigerator furnished with divisions (similar to the one M M, shown in fig. 49), in which a part of the vapour is condensed. D′ is the fifth chamber, of the same size as D, into which no steam is conducted: *i i* is a refrigerator similar to *f f*. The total capacity of the five chambers is therefore upwards of 100,000 cubic feet. These chambers receive every twenty-four hours the gas produced by the combustion of about 1 ton and a half of sulphur. F F is a series of carboys charged with sulphuric acid of sp. gr. 1·711. G is a box with perforated divisions for regulating the draught.

Conduct of the Chamber Process.—When a chamber system has to be set in operation, this is effected in the following manner. Sulphuric acid, of sp. gr. 1·357, is poured upon the floor of the principal chamber, in quantity sufficient to shut out the external air completely from the interior of the chamber. Water is not to be recom-

mended for this purpose, both on account of its absorbing sulphurous and nitrous acids, which attack the leaden floor, and also on account of its partly decomposing nitrous anhydride with evolution of nitrogen oxide. As soon as sulphuric acid in sufficient quantity has been poured into the principal chamber, sulphurous oxide is passed from the burners into the chamber. When the air has been displaced from the chamber the supply of nitric acid or of vapours of nitric acid to the chambers is commenced as above described, an excess being employed at the beginning. The temperature of the chambers is gradually raised by the hot gas, and as soon as it is perceptible through the sides of the chambers, the supply of nitric acid or of nitrous vapour is reduced to the normal standard. Earthen plugs fitted into the chamber in various parts serve by an inspection of their surface as a guide to the stage at which the process has arrived, and when the proper point is attained, steam is then passed into the chambers.

Introduction of Sulphurous Oxide.—The relation of the amount of sulphur to the surface of the chambers has been already sufficiently treated of. Where non-continuous burners are employed the sulphur must be thrown in in small portions, at intervals of an hour at a time. The temperature of the sulphur furnace should never be allowed to rise too high, as thereby the sulphur is apt to burn too rapidly, and too much sulphurous oxide is sent into the chambers. A reduction of the temperature of the furnace is effected either by reducing the draught, or by less frequent charging, etc. of the burners. As a matter of course the regulation of the process is easier in proportion to the number of burners employed.

The Supply of Atmospheric Air.—This depends upon the quantity of sulphur burnt. Sulphur requires for its combustion to sulphurous oxide (SO_2) its own weight of oxygen, and for oxidation to sulphuric anhydride (SO_3) half as much more; so that it would require the oxygen contained in rather more than six and a half times its weight of atmospheric air. But since the oxygen of the air admitted is not perfectly absorbed, some excess of air is used containing oxygen amounting to six-tenths the weight of the sulphur burnt. Accordingly every pound of sulphur requires 1 + 0·5 + 0·6 = 2·1 pounds of oxygen in the form of atmospheric air. Assuming that 1 cubic foot of atmospheric air at a temperature of 0°, and under a pressure of 760^{mm} of mercury, contains ·21 cubic foot or 0·187 pound of oxygen, the above 2·1 pounds would correspond to a volume of air equal to 113 cubic feet.

The admission of air is generally regulated by sliding doors attached to the burners, and sometimes by means of a special apparatus which admits of the air being measured and regulated.

The Supply of Steam.—This may be estimated as follows: The chamber acid, when it has a strength corresponding to sp. gr. 1·530, contains 51·1 per cent. of sulphuric anhydride, corresponding to 20·44 sulphur and 48·9 water. Accordingly every 20·44 parts of sulphur requires for its conversion into acid of sp. gr. 1·530, 48·9 parts of water, or, what is the same, 1 part of sulphur requires theoretically 2·392 parts of water. But since a portion of the water employed is invariably carried off with the other gases, it is usual to pass into the chambers 2·5 or 3 parts of water in the form of steam, for every part of sulphur burnt.

Chamber Crystals.—When vitriol chambers are worked with an insufficient supply of moisture, this compound is always formed. Its production is consequently a result of bad management. Different views are held as to the composition of these crystals. According to Weltzien and R. Müller, it is a compound of nitrogen peroxide with sulphuric acid ($2H_2O$, $3SO_3$, $2NO_2$); according to Weber it is a compound of sulphuric acid with nitrous anhydride ($H_2SO_4 + N_2O_3SO_3$). Considering the various ways in which this substance has been prepared artificially, it is easy to understand its formation in vitriol chambers. Thus, it has been formed by the reaction of sulphurous oxide and nitrogen peroxide at a moderate temperature in presence of water; by the action of nitrogen peroxide upon sulphuric acid monohydrate; by mixing red fuming nitric acid with concentrated sulphuric acid; by conducting nitric oxide gas and air simultaneously into sulphuric acid; by bringing together sulphurous oxide, nitric oxide gas, air, and a small quantity of steam; by conducting sulphurous oxide into very concentrated nitric acid, or into a mixture of nitric and sulphuric acid, etc.

Although it seems most probable that the crystals are formed in the lead chambers by the mutual action of nitric oxide, sulphurous oxide, air, and steam, this by no means excludes the possibility of the crystals being formed, under certain conditions, by one or other of the reactions above given.

The substance is deliquescent; it is soluble in concentrated sulphuric acid; less so in nitric acid. It is decomposed in contact with an excess of water into sulphuric acid and nitric acid, evolving at the same time copious red fumes of nitrous anhydride. This action of water upon the chamber crystals is of great practical importance,

because it affords a means of effecting the decomposition of this substance, even when dissolved in sulphuric acid. When it has been formed in the chambers, the admission of steam suffices for the purpose.

It is evident, from the foregoing, that in the manufacture of sulphuric acid great care must be taken to maintain the right proportion between sulphurous oxide, nitric acid, air, and water. When too much sulphurous oxide is present it escapes into the chimney unoxidised; when nitric acid is used in excess, nitric oxide, nitrous anhydride, etc. are also carried into the chimney with the residual nitrogen of the air; when insufficient water is present, chamber crystals are formed, and, finally, when too much air is sent into the chambers, the gases have not sufficient time for reacting upon one another, and thus escape in part unaltered.

The temperature most suitable for the formation of sulphuric acid is between 40° and 60°. It is regulated either by the rate of admission of steam or by the extent to which the sulphurous oxide is heated.

Introduction of the Nitric Acid.—At the beginning of the operation the calculated quantity of nitric acid required is about 10 or 15 per cent. of the weight of sulphur burnt; during the process, however, the quantity of nitric acid necessary is reckoned at about 5 or 6 per cent. Theoretically, when the process is once in operation, no further addition of nitric acid ought to be required; but in reality oxides of nitrogen are carried away in such quantity by the residual nitrogen of the air that a continual supply of fresh nitric acid is necessary. If a cheap method of preparing oxygen gas were known, it would be possible not only to effect a great saving of nitric acid, but at the same time the operation of manufacturing sulphuric acid might then be conducted in very much smaller chambers.

Temperature of the Chambers.—The proper regulation of the temperature of the chambers is a matter of great importance. The process of sulphuric acid manufacture is found to be most successful when a thermometer placed at a distance of 5 feet from the floor of the principal chamber shows a temperature of 40° or 44°. The temperature, however, in the interior of the chambers varies far more, fluctuating between 40° and 60°. The other chambers are also furnished with thermometers. The regulation of the temperature in the chambers is effected by increasing or diminishing the supply of nitric acid or nitrous gas; the greater the quantity of nitric acid admitted in a given time the higher is the temperature. In order to prevent the sulphurous oxide from entering the chambers too hot, the gas from the burners is first conducted either through a brickwork flue, or, in some sulphuric acid works, through condensers kept cold by a stream of water.

In judging as to the proper course of the process, two points have to be considered, viz. the specific gravity of the chamber acid and the character of the chamber gas.

The Specific Gravity of the Chamber Acid.—For the purpose of determining this, funnel-shaped arrangements of lead (A A, figs. 72 and 73), placed about 3 feet above the floor of the chambers, are attached to the chambers in different parts. These serve to collect the sulphuric acid as it trickles down the sides of the chambers, the acid flow-



Fig. 72.



Fig. 73.

ing out through the tube (A') which passes through the wall of the chamber into the vessel (B), containing an hydrometer, and then flowing back again into the chamber through the tube (*d*).

The Character of the Gas.—This is determined by the odour and colour. The first is ascertained by test tappings, the latter by means of windows set opposite one

another in the sides of the chambers. The colour of the escaping gas is likewise determined either by the aid of windows placed opposite one another, or by wide glass tubes. The gas ought to have a reddish-yellow colour. If the coloration is too light, sulphurous oxide and sulphuric acid are apt to escape; if too dark, too much nitric acid has been employed. In the former case the supply of nitric acid must be increased.

Determination of the Absorption of the Nitrous Gases in the Coke Tower, or other Condensing Arrangements.—This is most advantageously effected by means of Hart's titration method, which depends upon the fact that urea and nitrous anhydride decompose one another, forming water and nitrogen. When, therefore, a small quantity of the sulphuric acid to be tested is dropped by means of a burette into a solution containing a definite quantity of urea, paste containing potassium iodide is not coloured blue by the solution so long as undecomposed urea is present, as the nitrous anhydride which is the cause of the blue coloration is decomposed by it. The amount of nitrous anhydride in the sulphuric acid to be examined may therefore be easily determined by the quantity of such sulphuric acid necessary for the decomposition of a known quantity of a solution of urea.

Concentration of Sulphuric Acid.—This operation is conducted in two stages: first, the concentration in open lead pans to sp. gr. 1·752, and then the concentration up to sp. gr. 1·842, in vessels of platinum or glass, other substances not being able to resist either the action of the hot acid or the high temperature.

An apparatus for concentrating sulphuric acid which is much used is shown on fig. 74. It consists of two leaden pans (A and B) supported on cast-iron plates, and

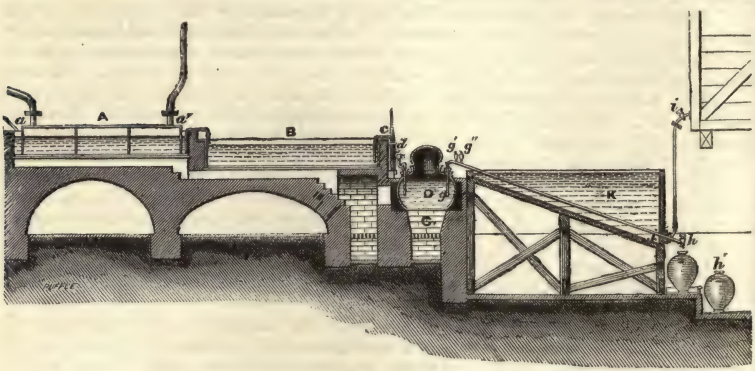


Fig. 74.

heated by the hot air from the furnace (C). Immediately above C is a platinum retort (D), into which flows the acid that has been concentrated in the pan (B) to sp. gr. 1·752, and is therein heated to the boiling point. Platinum is not acted upon by either cold or boiling sulphuric acid; its melting point (1800° – 1900°) is far above the boiling point of concentrated sulphuric acid, which is only 338°. However, the platinum vessels used for concentrating sulphuric acid are often considerably corroded, partly by the action of oxides of nitrogen, and partly by chlorine, when the saltpetre used in the nitre pots contained sodium chloride.

The sulphuric acid is run from the chambers through a leaden tube into the pan (A), where it is often submitted to a process of purification, consisting in a treatment with sulphurous oxide gas while in a hot state, the oxides of nitrogen being thus reduced, and the sulphurous oxide itself converted into sulphuric acid. For this purpose the pan (A) has a lid made of sheet lead arranged bell-like over the sulphuric acid in it. The four vertical sides close the apparatus hermetically, while the partitions inside do not quite reach the sides, and so the sulphurous oxide gas, entering at *a*, has to pass backwards and forwards, and comes as much as possible in contact with the sulphuric acid.

The sulphurous oxide used for this purpose is drawn from the sulphur burner (A, fig. 48) and passed through a tube (*a*, fig. 74) under the leaden lid above mentioned. It then circulates over the heated sulphuric acid, any excess of it escaping, together with nitric oxide and nitrous oxide thus formed and the steam carried over, through *a* into the wide leaden tube (D, fig. 48), whence the gas passes into the chamber (E). In order to draw the sulphurous oxide from the burner through the entire apparatus, a

steam aspirator is fitted at D, fig. 48, consisting of a steam-pipe an inch in diameter, from which steam is ejected through an opening one fifth of an inch in diameter at a tension of about two atmospheres. The sulphuric acid flows from the pan (A) through a syphon into a second pan (B), where a further concentration to about sp. gr. 1·750 is effected. In this pan the last portions of oxides of nitrogen are often destroyed by the addition of from ½ to 1 part of ammonium sulphate per 1000 parts of acid. The sulphuric acid then flows through a syphon (*c*) into the regulator (*d*), the interior arrangement of which controls the flow of acid into the still (D). This regulator consists of a cylindrical vessel (*d*), with an outflow pipe about half-way up the side, and supported upon chains to admit of being drawn up or lowered at pleasure. The level of the acid in which the end of the syphon terminates is thus raised or lowered; the flow of sulphuric acid into the funnel of the platinum retort is accordingly made quicker or slower, or stopped altogether.

Often, instead of two lead pans, three or four are arranged terrace-like one above the other, and they generally have a separate furnace. It may be here mentioned that the first concentration is in many works effected by passing the gas from the furnace through a brickwork chamber above the surface of the acid in the evaporating pans.

The final concentration of sulphuric acid is generally carried out in platinum stills; a distinction being made between intermittent and continuous working.

In intermittent working the platinum still (D, fig. 74) is three quarters filled with acid, the quantity of acid poured in being observed by means of a platinum float, and as soon as about two tenths of the liquid has distilled over, a further quantity of acid is run into the still. The vapour of the boiling acid escapes through the head of the still (D) into a condensing worm at the side not shown in the drawing, where it is condensed and flows into a leaden reservoir.

The distillate thus obtained contains at first a great quantity of water and very little acid, but in proportion as the acid in the still becomes concentrated, and its boiling-point rises, a stronger acid distils over, and it would be possible in this way to raise the temperature so high that at last pure acid would distill over. It is, however, not customary to raise the temperature of the acid in the platinum still so high as this, except when an extra concentrated acid is required. This acid ought to have a specific gravity of 1·842.

On account especially of the high temperature required in the production of this acid, the reduction of temperature caused by the flow of much cooler acid from the leaden pans is so great, that the sides of the still contract very considerably, often producing cracks in the still, after a number of operations have been carried out. The sulphuric acid is distilled generally only up to the point where the distillate shows a specific gravity of 1·152. Payen represents this acid distillate as having a specific gravity of 1·420, and it would be therefore stronger. The acid remaining in the platinum still shows a specific gravity of 1·846.

The Continuous Process.—This process, in which the acid is kept continually flowing in and out of the platinum vessel, is as a rule to be preferred to the intermittent process. By the continuous process an acid is obtained which has a specific gravity of only 1·819, but for most purposes it is as good as the acid of sp. gr. 1·848. The continuous process has this further advantage, that about half as much acid again is produced as by the intermittent process; and owing to the level being constant in the platinum stills, no sudden cooling is apt to take place, the platinum stills being on this account far less attacked.

When the sulphuric acid has attained the desired degree of concentration, it is drawn off with a platinum syphon (*g g′ g″ h*, fig. 74) reaching to within a distance of one third of an inch from the bottom of the still. In order to set the flow of acid going, both the platinum plugs *g′g′* are removed, and sulphuric acid poured through one of the two small funnels into the long arm of the syphon; the other funnel serves for the escape of the air. As soon as the syphon arm is full up to the mouth of the funnel the platinum plugs are again fitted in, and the cock *h* opened, whereupon the concentrated acid flows out into carboys. Since the acid as it comes from the platinum retort has a high temperature, it is necessary to cool it before running it into the carboys, so as to avoid cracking them. For this purpose it is passed through a tube fitted into a condenser, the latter being so arranged that cold water is kept flowing in at its lowest point, and the heated water is let off above. Other forms of apparatus something like a Liebig's condenser are sometimes used, the limb of the syphon passing through a large tub (K) filled with water. The syphon limb has often several branches, so as to increase the cooling surface. In such a case, however, the branches all taken together do not represent a greater sectional area than the syphon at its upper or lower end, where the branches unite. Other contrivances consist in allowing the acid to flow from the syphon through a funnel into a worm condenser, whereby the cooling

is very thoroughly effected. When it is desired to despatch the carboys as soon as filled, a float of glass or platinum is placed in the mouth of each carboy extending beyond its neck, and connected with a mechanical arrangement which sets a bell ringing as soon as the acid in the carboy has risen to within $1\frac{1}{2}$ or 2 inches of the mouth of the carboy, thereby intimating to a workman when it is necessary to close the cock and remove the carboy.

An improved apparatus introduced by Chapuis, Demoutis, and Quenessen, is represented by figs. 75 and 76. The platinum still rests upon a bed of fire bricks, and is heated by the hot air from the furnace (E) circulating round the still in the flues (o o'). The still is fitted with a head (A), through the neck of which the vapour is conducted into a leaden condensing worm (E S S E). The hollow globular vessel (E) is kept continually half filled with condensed acid, and is consequently not attacked by the acid dropping into it from the still. The continual influx of acid of sp.gr. 1·580 is here also effected by means of the apparatus (*d*, fig. 74). From this the acid flows into the funnel (*b*) fitted with a dropping arrangement with holes (*c*), which serves to distribute the acid over the interior and heated sides of the still, by which it is considerably concentrated before it gets to the remaining contents of the still. On the other side of the still is fitted a syphon (*t t*) for the removal of the concentrated acid, which runs off in a continual stream. The process of clarification, cocling, and filling into carboys is considerably

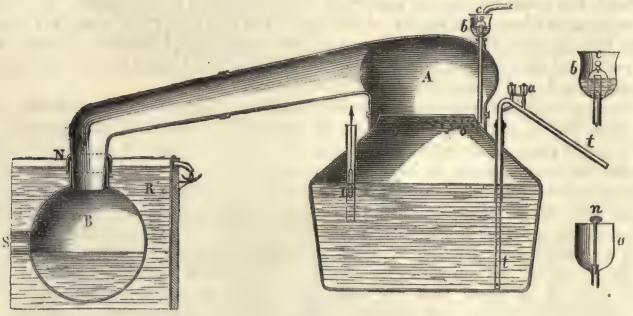


FIG. 75.

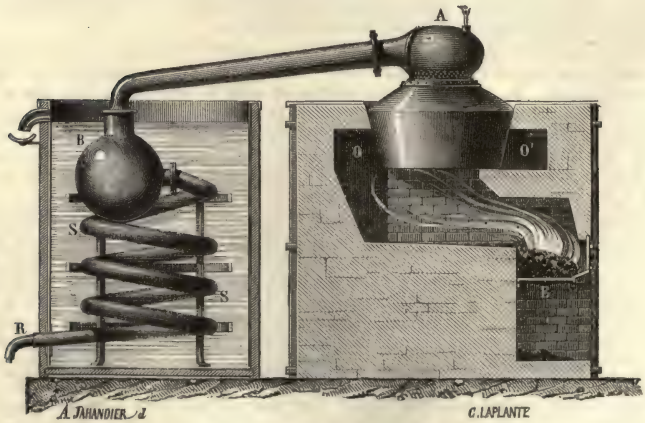


FIG. 76.

assisted by the use of the apparatus shown in fig. 77. The acid flows from the end of the cooling syphon through the cock *b* into a number of Woulfe's bottles (*c' c'' c''' c''''*), arranged in a long trough filled with cold water, and communicating with one another by means of syphons (*d d' d''*). A fourth syphon (*d'''*) of platinum closed by the cock (*e*) serves for drawing off the cooled acid into carboys for exportation. For the sake of sparing platinum and thereby rendering the whole apparatus cheaper, these stills are

sometimes constructed with a leaden head fitting upon the platinum vessels. The upper edge of the platinum still is then bent round over an iron gutter, and the conical

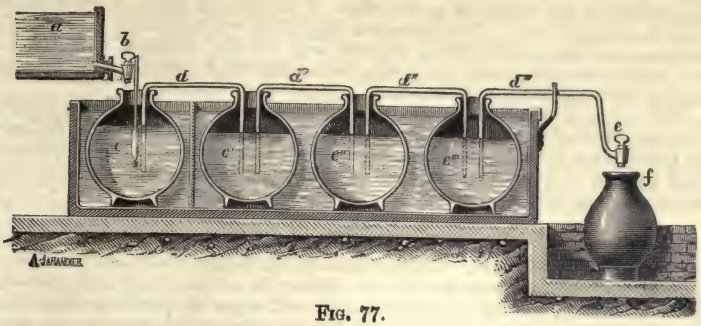


FIG. 77.

leaden head fits into this gutter and closes the retort with an hydraulic joint. At present a suitable cooling apparatus is wanting for the leaden cap, which, when too hot, sinks in by virtue of its own weight. A cap with double sides, between which the chamber acid might be made to flow, so as to give it the required temperature, would possibly remove the difficulty.

An apparatus entirely of platinum costs several thousand pounds. With an apparatus of this kind as much as four tons of ordinary sulphuric acid may be produced daily. The daily wear and tear and interest on first cost is, however, less than the cost involved in the use of the glass retorts in many cases, apart from the risk incurred by the workmen when they are used. The conditions are still more favourable where platinum stills are employed in the continuous process.

Concentration of Sulphuric Acid in Glass Retorts.—At the time when the manufacture of sulphuric acid was in its infancy, the acid was concentrated in large glass retorts of ordinary form, each retort being set upon a sand bath. A number of retorts, varying from ten to twelve and more, were placed in a double row and heated by a single fire. Each retort was connected by an adapter with a carboy, into which the weaker acid distilled over. This arrangement was simplified, and the consumption of fuel reduced by covering the retorts with a coating of clay before heating them.

This apparatus is still in use in several places, as, for instance, in the neighbourhood of Montpellier, and generally in the vicinity of glass works, where large retorts are cheap. Platinum apparatus has of late met with severe competition from glass retorts of a new kind. These glass vessels are cylindrical in shape, their bottoms arching outwards; they are furnished above with a neck, into which one end of the delivery tube fits tightly, while the other end dips into a leaden receiver for collecting the distilled acid. The glass vessel stands in a sand bath, the bottom of which alone is covered with sand, each sand bath being heated by a separate fire, the flame impinging round the bath on all sides. When the concentration has proceeded far enough the tubes connecting the retort with the leaden receivers are removed, and the acid drawn off from the retorts with a syphon. The retorts are then again filled with acid previously made hot. A retort of the kind holds about 30 gallons, and it yields at each operation 3 cwts. of concentrated acid. Balloon-shaped vessels have also recently been employed in the concentration of sulphuric acid.

Great attention to the most suitable construction of the glass retorts has led of late to such perfection in their manufacture that in some localities the cost of working them is less than that involved in the use of platinum stills.

Several other methods of concentrating sulphuric acid have been proposed, none of which have met with success, and on this account they need only cursory mention. Kuhlman and Keller recommend concentrating sulphuric acid in vacuum, so as to reduce the boiling point of the acid and enable vessels of lead to be employed. It has, however, been found that notwithstanding the reduction of the boiling point, the leaden vessels are far too much acted upon to render this method practicable. Clough proposed concentrating the acid in leaden pans, kept cool by a constant current of cold water; the removal of water from the acid being effected by passing heated air from a furnace over the surface of the acid. Gossage suggested a method according to which the acid is allowed to trickle down over flints piled up in a high tower, hot air being passed through the flints in an opposite direction.

Purification of Chamber Acid.—The chamber acid generally contains impurities derived from the raw materials used in its preparation, and when it has to be concentrated is first submitted to a process of purification which is often combined with the concentration. The commonest impurities are sulphurous acid, selenium, thallium, lead, organic substances, arsenous acid, and the oxides of nitrogen (nitric acid, nitrous anhydride, etc.) As a rule, the purification is limited to the removal of the last-mentioned substances.

The Oxides of Nitrogen.—Nitric acid, nitrous anhydride, etc., would be destroyed when sulphuric acid is deprived of its arsenical impurities by sulphuretted hydrogen; but if this is not done they may be easily removed by adding to the sulphuric acid a small quantity of ammonium sulphate. On the application of heat, ammonia reacts with the nitrous anhydride according to the following equation:

$$2NH_3 + N_2O_3 = 4N + 3H_2O.$$

The oxides of nitrogen may be also completely removed by heating the sulphuric acid with a little oxalic acid. Carbonic oxide is thus formed which acts as a reducing agent upon the oxides of nitrogen. Nitric acid may be got rid of most easily according to Wackenroder by heating the sulphuric acid with sugar or starch, or according to Barruel with some sulphur. By treatment with sulphurous oxide gas alone the greater portion of the oxides of nitrogen may be removed.

Chamber acid, having as it comes from the chambers a sp. gr. of 1·535 to 1·550, may be concentrated to sp. gr. 1·583, and at the same time freed from the oxides of nitrogen by means of the arrangement shown in section and projection by figs. 78 and 79. The chamber acid passes through the tube (*a*) into a lead pan (*b b b*), surrounded by brickwork (*c c c*). The acid flows slowly round the tongue (*d d*) towards the tube (*e*), through which it passes into the lead pans next the platinum still. On its way the sulphuric acid meets with a stream of sulphurous oxide and air passing in a contrary direction, as shown by the arrows, fig. 79. The sulphurous oxide is prepared in the furnace (*f*) by burning sulphur, and it passes, mixed with air, through the cast-iron tube (*g g*) into the chamber (*h h*), where the greater portion of the sulphur vapour condenses. From thence it takes the way above mentioned, passing over the sulphuric acid, abstracting from the latter some of its moisture, and destroying the nitrous admixtures, escaping finally through the tube (*i*) into the first vitriol chamber.

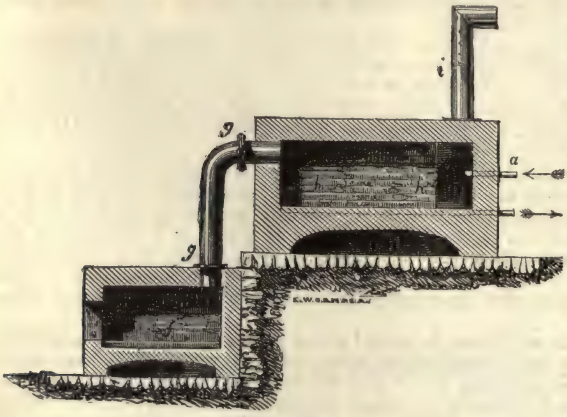


Fig. 78.

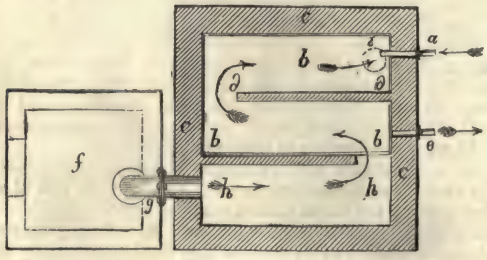


Fig. 79.

Arsenous acid may be got rid of by conducting sulphuretted hydrogen gas into the acid diluted to sp. gr. 1·420, accelerating the action by the application of heat, and filtering off the arsenous sulphide. The sulphuretted hydrogen is either prepared by the action of dilute sulphuric acid upon iron sulphide, or, according to Du Pasquier's method, it is evolved in the acid to be purified by throwing in some pieces of barium

sulphide. Sulphuretted hydrogen may also be produced by the action of carburetted gas upon red-hot pyrites. When the arsenic in sulphuric acid is in the form of arsenous acid alone, it may be easily got rid of by Buchner's method. For this purpose the arsenic is converted into arsenous chloride by passing hydrochloric acid gas into the sulphuric acid; by subsequently heating the acid to a temperature of 132° the volatile arsenous chloride is driven off. When arsenic acid is present, it must be reduced to arsenous acid by passing into the acid to be purified sulphurous oxide gas, or heating it with some charcoal before treatment with hydrochloric acid.

Attempts to utilise atmospheric air for the oxidation of sulphurous oxide by conducting a mixture of the two over porous substances, such as mixtures of clay with the oxides of iron and chromium, or of copper and chromium oxides, pumice, etc., have not as yet led to any useful results, and no method has yet been devised which would supersede the indirect oxidation of sulphurous oxide by nitric acid, and the use of large leaden chambers for bringing about the reaction.

Wöhler and Mahla suggested conducting a mixture of sulphurous oxide and air over red-hot oxides, such as a mixture of copper and chromium oxides, etc. Petrie suggested that a mixture of sulphurous oxide and air at a temperature of 300° should be passed upwards through a high tower filled with pieces of granite kept moist with water. Persoz proposed passing sulphurous oxide into diluted nitric acid, by which the sulphurous oxide is converted into sulphuric acid and remains in solution, while the nitrogen peroxide formed escapes, and may be again converted into nitric acid by the action of air and water. In this reaction the nitric acid may be replaced by a nitrate mixed with hydrochloric acid. In the latter case nitrogen oxydichloride is formed, which by the action of air and water is, like nitrogen peroxide, reconverted into nitric acid. Hahner and Macfarlane suggest oxidising sulphurous oxide by chlorine in the presence of steam.

But although such methods have not yet been rendered practicable on the large scale for the production of sulphuric acid, the oxidation of sulphurous oxide by atmospheric air, and without the intervention of nitric acid, has been so far successfully applied by Hargreaves in the direct production of sodium sulphate from sodium chloride, that his method promises to do away with the necessity for sulphuric acid in the manufacture of soda, for which purpose greater part of the sulphuric acid now made is used. So far as this manufacture is concerned therefore, the adoption of Hargreaves' method would render the use of lead chambers unnecessary. (See 'Soda Manufacture.')

Methods have also been proposed for separating the sulphuric acid contained in gypsum, Frémy suggesting heating gypsum with sand, and Tilghman proposing to pass steam over red-hot pieces of gypsum, the products in both cases being passed into the lead chambers. Köhsel suggests heating gypsum with charcoal, thus forming carbonic acid and calcium sulphide. The carbonic acid hereby evolved is made to decompose a solution of calcium sulphide from a former operation, the sulphuretted hydrogen thus formed being burnt, and the gaseous product conducted into the lead chambers. A number of other propositions have been made for making use of gypsum as a source of sulphuric acid, which for want of space cannot be detailed here.

Uses.—Sulphuric acid is used in the preparation of most other acids, as, for instance, sulphurous, hydrochloric, nitric, phosphoric, boracic, fluoric, tartaric, citric, stearic, and other fatty acids.

Sulphuric acid is employed in the preparation of most sulphates, such as those of sodium (Glauber's salt), potassium, ammonium, aluminum, iron, copper, magnesium (Epsom salt), mercury, the latter being again used for the preparation of mercury chloride (corrosive sublimate), and protochloride (calomel); alum also is indirectly prepared by the agency of sulphuric acid.

Sulphuric acid in a diluted state is used for dissolving iron and zinc; the hydrogen thus evolved being employed for filling air balloons, for Döbereiner's fire apparatus, for the oxhydrogen flame used for melting purposes and for illuminating microscopic objects, also for the detection of arsenic in Marsh's apparatus. Diluted sulphuric acid is also made use of in exciting an electric current between zinc and copper and other substances, for electro-plating, telegraphic and other purposes.

Sulphuric acid is further a valuable reagent in the hands of the chemist, in alkalimetrical and acidimetrical determinations, in the quantitative determination of barium and lead, etc. Sulphuric acid is also used for cleaning the surface of iron plates; in the manufacture of tin plate and galvanised iron; for cleaning copper and silver before coining; for refining of gold and silver; for separating gold from alloys of copper; further, in the dissolving of indigo. It is also used in the preparation of ether, madder dyes, in the purification of various oils, for giving a dark colour to wood, in the manufacture of blacking, of sugar from starch, and

for preparing guncotton, collodion, nitrobenzol, nitroglycerin, picric acid and its salts, vegetable parchment, etc. Sulphuric acid mixed with from 20 to 30 times its weight of blood coagulates and preserves it; it also acts in the same way upon urine, preventing in it the unpleasant alkaline fermentation, and is on this account used for disinfecting purposes. Sulphuric acid is also used for precipitating the lime from molasses, for extracting fats from woollen or cotton goods, for separating out the pure hydrocarbons and other constituents from different kinds of tars. Sulphuric acid is also very effective for the removal from casks or vats of bad smells caused by fungoid growths, such vessels being treated for a short time with sulphuric acid and afterwards rinsed out with clean water to remove adhering acid.

A very extensive use is now made of sulphuric acid in the manufacture of superphosphates, for converting the insoluble calcium phosphate of various substances into a soluble condition. The manufactories of superphosphates at Barking, Plaistow, Deptford and Birmingham consume annually several thousand tons of sulphuric acid in the manufacture of superphosphates.

Finally, sulphuric acid is extensively employed as a drying agent in chemical laboratories, in virtue of its strong hygroscopic properties.

SULPHURETTED HYDROGEN.

FORMULA H_2S. MOLECULAR WEIGHT 34.

History.—Although this gas must have been frequently observed by the old chemists, its existence as a distinct substance was not recognised until the seventeenth century, and it was not until the end of the eighteenth century that its chemical nature was definitely established by Berthollet.

Occurrence.—Sulphuretted hydrogen often occurs naturally in the water of springs. The best known of the sulphuretted springs are those of Harrogate, Aix-la-Chapelle, Baden near Vienna, Eilsen, Burtscheid, Bagnères, Baréges, etc. Sulphuretted hydrogen is also found wherever nitrogenous organic substances containing sulphur, or in contact with sulphates, are undergoing decay.

Characters.—Sulphuretted hydrogen is, at ordinary temperatures, a colourless gas; its density as compared with hydrogen gas is 17, and its specific gravity relatively to atmospheric air is 1·1912. When submitted to a pressure of 16 atmospheres, sulphuretted hydrogen gas condenses to a colourless mobile liquid, having a specific gravity of 0·9 as compared with water, and this solidifies to a crystalline mass at a temperature of $-85°$. Sulphuretted hydrogen has a penetrating, disgusting smell, resembling that of rotten eggs: it is irrespirable, very poisonous, and combustible, burning with a bluish flame, the products of its combustion being sulphurous oxide and water. Sulphuretted hydrogen imparts a wine red colour to the blue colouring matter of vegetables, a property which it shares in common with boracic, carbonic, and other weak acids, and on this account it is also called hydrosulphuric acid. When passed through a tube heated to redness, sulphuretted hydrogen is decomposed with deposition of sulphur. Water dissolves from 2·5 to 3 times its volume of sulphuretted hydrogen gas. The solution is clear when freshly prepared, but gradually becomes muddy by keeping, owing to the separation of sulphur as a result of partial oxidation. For this reason sulphuretted hydrogen water requires to be kept in well-stoppered bottles.

Sulphuretted hydrogen absorbed by humus or other porous substances decomposes in contact with air, its hydrogen oxidising to water, while sulphur is at the same time set free. When a mixture of sulphuretted hydrogen and air is heated in contact with porous bodies to $40°$—$50°$, a portion of the sulphur is oxidised as well as the hydrogen, water and sulphuric acid being formed.

Sulphuretted hydrogen is an unstable substance; chlorine readily abstracts its hydrogen, forming hydrochloric acid and liberating sulphur, which then combines with chlorine when it is present in excess. Chlorine is therefore employed as an antidote in cases of poisoning with sulphuretted hydrogen. Bromine and iodine act in a similar manner upon sulphuretted hydrogen. Fuming nitric acid decomposes sulphuretted hydrogen with explosive violence. Sulphuretted hydrogen is decomposed by most metals with the aid of heat, hydrogen gas being liberated and a sulphide of the metal formed. The property possessed by sulphuretted hydrogen of precipitating several metals in the form of sulphides from solutions of their salts renders it a very valuable reagent in analytical operations.

Preparation.—When required on a small scale, sulphuretted hydrogen is generally prepared by pouring dilute sulphuric acid or hydrochloric acid upon pieces of ferrous sulphide contained in a good-sized glass flask. The reaction is represented by the following equation:

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The gas is passed through a Woulfe's bottle, containing some water, to free it from any particles of acid carried over with the stream of gas.

For the preparation of sulphuretted hydrogen free from uncombined hydrogen, it is better to use antimonous sulphide, instead of ordinary ferrous sulphide which always contains some metallic iron that gives rise to evolution of hydrogen. The crude antimonous sulphide of commerce suffices for this purpose, and hydrochloric acid is used for decomposing it.

Sulphuretted hydrogen is also prepared on a large scale from ferrous sulphide and dilute sulphuric acid. The ferrous sulphide is obtained by melting together 28 parts of iron scraps with 16 parts of sulphur in graphite crucibles two feet high. At Oker the ferrous sulphide is prepared by melting together 2 parts of iron pyrites poor in copper with 1 part of copper ore slag, containing about 50 per cent. iron and 1 per cent. copper. The excess of sulphur of the iron pyrites combines with the iron of the slag, forming ferrous sulphide. Upon treating the product with acid, the copper sulphide remains unaltered. A similar method is employed at Freiberg.

The ferrous sulphide obtained in either of the above ways is placed in leaden vessels and covered with dilute sulphuric acid, the sulphuretted hydrogen evolved being passed before using through a vessel containing water.

Weltz's method of preparing sulphuretted hydrogen depends upon the fact that hydrogen and hydrocarbon gases in contact with red-hot iron pyrites yield sulphuretted hydrogen. The gas employed for this purpose is obtained by imperfect combustion of fuel, conducted in such a way that the air supplied for the combustion, instead of ascending through the burning material, is made to pass downwards through the heated fuel and thus produce, by the heat generated, a kind of distillation of the unburnt fuel, by which means the gas becomes charged with hydrogen and carburetted compounds.

The generator employed has the form of a shaft furnace; it is completely filled with charcoal, which is ignited above the grate, and while the furnace is open above, air is blown in from below, so as to bring the entire mass to a red heat. The generator is then well closed above and the gas is compelled to pass downwards through the grate and through a brick flue, into the pyrites furnaces. The pyrites furnaces are built of fire bricks, and are entirely filled with pyrites. The gas from the generator enters the pyrites furnaces through a fire bridge, through which air is passed at the same time, sufficient to cause partial combustion of the gas and the heating of the pyrites up to the temperature required for its decomposition by the unburnt gas in the manner already mentioned.

Uses.—Sulphuretted hydrogen is employed principally as an analytical reagent in chemical laboratories, in a state of solution as well as in the gaseous state. It is used in qualitative analysis for separating one group of metals from another, the metals of the one group being precipitated by it from acidulated solutions of their salts, while the metals of the other group are not precipitated, but remain in the filtrate.

Sulphuretted hydrogen is also often employed in quantitative analysis and for the preparation of ammonium sulphide and potassium sulphide, etc.

Sulphuretted hydrogen is used on a large scale for removing arsenic from sulphuric acid, for precipitating copper from solutions of the salts of that metal, and for precipitating gold in the extraction of gold and silver, from waste materials containing them, by the chlorine process.

CARBON BISULPHIDE.

FORMULA CS_2. MOLECULAR WEIGHT 76.

History.—Bisulphide of carbon was accidentally discovered by Lampadius, in 1796, while heating charcoal to redness with pyrites. He described the properties of the body, but he did not succeed in obtaining it again according to the old method until 1803. Meanwhile Clément and Desormes obtained the same substance by the action of sulphur upon charcoal, and named it *sulfure de carbone*. Its composition was long disputed. Berthollet asserted that the compound obtained by Clément and Desormes contained no carbon, but consisted of sulphur and hydrogen only, and Vauquelin ex-

pressed the same opinion. In 1811 Cluzel laid before the French Academy a paper containing the results of experiments, according to which, carbon bisulphide was asserted to contain, besides carbon, nitrogen and hydrogen as well. The consequence of this assertion of Cluzel's was that Vauquelin began a new series of researches into the nature of the body, and eventually succeeded in establishing its true composition.

Characters.—Carbon bisulphide at the ordinary temperature is a mobile, strongly refracting liquid, having a specific gravity of 1·293. It is colourless, and has a peculiar unpleasant odour. The smell of commercial carbon bisulphide is, however, partly owing to its containing small quantities of sulphuretted hydrogen; it may therefore be got rid of by shaking the carbon bisulphide up with water containing hydrated oxide of lead suspended in it, decanting, and distilling; the sulphuretted hydrogen combines with the hydrated lead oxide, and the smell disappears. According to Cloez, it is better to make use of small pieces of mercuric chloride, in the place of hydrated lead oxide, the carbon bisulphide being shaken up with the mercuric chloride, and then slowly distilled in a water bath. Pure carbon bisulphide boils at 48°, the specific gravity of its vapour is 2·66. The latent heat of the vapour of carbon bisulphide is much less than that of steam. It follows, as a consequence of this, that carbon bisulphide vapour need be deprived of only a small quantity of heat in order to insure its condensation; and that on this account it is advisable to surround vessels from which carbon bisulphide is distilled with bad conductors of heat, otherwise a large quantity of the vapour condenses before getting into the condenser, and flows back into the distilling vessel.

When burnt, carbon bisulphide develops a heat equal to 3400 heat-units, less than half that of wood charcoal. It burns with a beautiful blue flame, yielding carbonic dioxide and sulphurous oxide, according to the equation:

$$CS_2 + 6O = CO_2 + 2SO_2$$

Its tension is so considerable that it takes fire at the ordinary temperature (18°–22° C.) when a burning body is brought near the surface of the liquid, it not being necessary, in order to cause ignition, that the burning body should come in contact with the liquid itself; a property which very much increases its dangerous nature. A mixture of carbon bisulphide with air explodes, under certain conditions, with great violence. For this reason, it is necessary to exercise great caution with vessels containing carbon bisulphide, for an explosion of a vessel containing this substance may very easily cause the contents of neighbouring vessels to take fire; and in addition to the danger arising from the explosion itself, suffocating gases are produced, such as sulphurous oxide and carbonic dioxide, as well as the unburnt nitrogen of the air.

Carbon bisulphide is almost insoluble in water, but is very easily soluble in alcohol, benzol, oil of turpentine, and other liquid hydrocarbons; it is an excellent solvent for iodine, ordinary phosphorus, and crystallised sulphur. Payen succeeded in freeing illuminating gas from carbon bisulphide, by passing the gas through vessels containing pieces of crystalline sulphur. In order to regain both the sulphur and the carbon bisulphide it was then only necessary to distill off the latter.

If a few drops of nitric acid be poured into a jar containing carbon bisulphide vapour, sulphur is deposited, and a reddish gas is formed; the reaction being accompanied by the appearance of a bluish white flame, a portion of the sulphur being oxidised to sulphurous oxide. Carbon bisulphide deports itself to some extent as an acid. It combines with metallic sulphides, such as potassium sulphide and sodium sulphide, etc., forming crystallisable salts. Brought into contact with the alkalies and soluble earthy bases, carbon bisulphide replaces the oxygen in them with sulphur, forming carbonic acid and metallic sulphides which combine with a further portion of carbon bisulphide, forming salts. It reacts in an analogous manner with the insoluble metallic oxides, when its vapour is passed over them at a red heat.

The characteristic coloration of a weak solution of iodine in carbon bisulphide is taken advantage of as a test for iodides. One tenth part by volume of carbon bisulphide is added to the liquid to be tested, forming according to the density of the liquid a well-defined stratum either above or below it. A few drops of chlorine water are then added to set the iodine free, and the whole well shaken. After standing for a moment, a beautiful violet coloration of the carbon bisulphide is observed; with traces of iodine the coloration is of a rose tint. Carbon bisulphide is not decomposed by boiling water under the ordinary pressure of the atmosphere: a fact of importance in the rectification of crude carbon bisulphide, and its use on a large scale.

Sulphuretted hydrogen dissolves readily in carbon bisulphide, forming with it, according to Zeise, an unstable chemical compound. The following substances are either partly or entirely soluble in carbon bisulphide, viz., the resins, the varieties of gum resin, the balsams, asphalt, camphor, wax, the fats and fatty acids, the acids of camphor, benzoic and cinnamic acids, paraffin, etc.

Owing to the great volatility of carbon bisulphide, great cold may be produced by its evaporation, and if this takes place very quickly under the air pump a cold of $-60°$ may be obtained.

Preparation.—Carbon bisulphide may be prepared on a small scale by means of the apparatus shown in fig. 80, consisting of a stoneware retort (A) with a tubulus

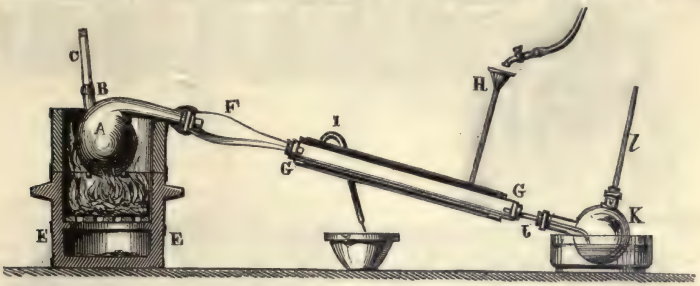


FIG. 80

(B), in which is fixed, by means of a lute consisting of clay and water, a porcelain tube (C) open at both ends. The retort is filled up to the neck with pieces of charcoal, placed upon a furnace (E) and fitted air tight with an adapter (F). This adapter is connected with a Liebig's condenser (G), the glass tube of which (J) passes into a doubly tubulated receiver (K). A glass tube (*l*) is fitted into the neck of the second tubulus of the receiver to conduct the uncondensed gases into a flue with a good draught.

When the whole apparatus has been proved to be air tight, the retort is heated to bright redness, and small pieces of sulphur are thrown into it, at intervals of about two minutes, through C; the porcelain tube being closed with a cork as soon as possible after each fresh addition of sulphur. According to the development of carbon bisulphide, which is observed in the adapter (F), the operator can judge of the rapidity with which sulphur is to be added.

The sulphur upon falling into the retort is volatilised, and coming into contact with an excess of charcoal at a high temperature, combines with it, forming carbon bisulphide. The product, which escapes very rapidly at so high a temperature, carries with it considerable quantities of sulphur. The vapour condenses partly in the adapter (F) and partly in the condenser (G), the liquid collecting in the receiver (K).

Care must be taken to insure a constant flow of water in the condenser (G), which consists of an outer metallic tube, through the axis of which is passed a long glass tube supported by perforated corks. The vapour which has to be condensed is passed through the inner glass tube, while the space between the two tubes is continually supplied with cold water by a funnel (H) near the lower extremity, while the hot water, being specifically lighter, escapes at the other end (I).

In order to free the carbon bisulphide collected in the receiver from sulphur, it is submitted to distillation in a glass retort over a water bath, the sulphur remaining in the retort. Carbon bisulphide thus treated is however not quite pure; it still contains sulphuretted hydrogen. To get rid of this, the carbon bisulphide is allowed to stand first of all in contact with hydrated lead oxide, then dried over calcium chloride, and finally distilled. Calcium chloride may be with advantage replaced by concentrated sulphuric acid, from which it is easy to separate the carbon bisulphide by means of a separating funnel.

By using the apparatus just described, it is easy to produce in a single day 40 ounces of carbon bisulphide, but the preparation in this way is seldom carried out, as carbon bisulphide is manufactured on a very large scale.

The preparation of carbon bisulphide for industrial purposes was introduced by Deiss and Jesse Fisher. The first forms of apparatus consisted of cast-iron cylinders, in which sulphur vapour was passed over charcoal heated to redness. A single cylinder yielded daily about 2 cwts. of carbon bisulphide. Fire-clay retorts were then employed, glazed internally, so as to prevent the escape of carbon bisulphide through their pores, and a number of such retorts were arranged in a furnace. An apparatus of the kind, as constructed by Deiss, is represented by figs. 81 and 82.

A is a furnace, containing four retorts (C) so arranged that the flame can play quite round them. The interior of the retorts is divided into two parts, by means of a perforated fire-clay plate; the upper part, which is the larger of the two, serves to

receive pieces of charcoal, thrown in through an opening in the lid; the lower part serves to receive the sulphur, which is thrown in through a somewhat conical tube

Fig. 81.

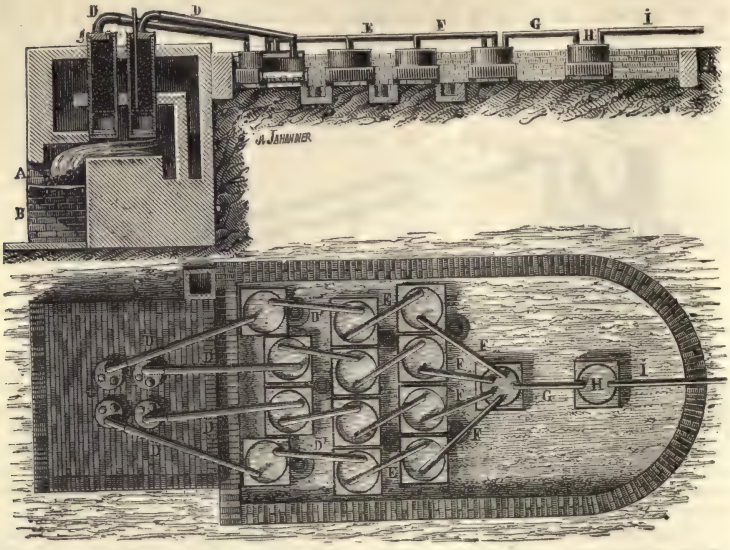


Fig. 82.

2 inches in diameter. The vapour formed upon heating the retorts passes through the pipes (D), which have a diameter of 3 inches, and then into the condensers.

A condenser of the kind is shown in section in fig. 83; as many as eighteen of them are connected together with tubes. The condensers are made of sheet zinc, and consist of a cylindrically shaped vessel, 26 inches in diameter, provided with perforations (*s s*) below, and standing in water in a trough up to the upper extremity of the perforations (*s s*). Two wide tubes pass through the lid of the cylindrical vessel into its interior, and serve for the transmission of the vapour. The lid is further furnished with a rim (*c*), 4 inches high, into which water is poured in order to cool it. The contents can either be removed from each receiver separately by means of a syphon, or the entire number of receivers are so connected with one another, that it is only necessary to draw off the liquid from the last one.

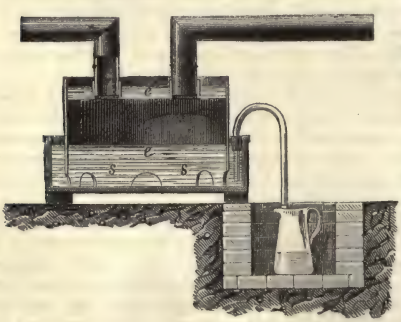


Fig. 83.

The process of manufacture is the following:—The four retorts are filled with charcoal, and then, after closing the openings through which the charcoal was introduced, the retorts are heated to bright redness by a coal fire. The next operation consists in dropping pieces of sulphur, done up in cylindrical paper packets, through the tube which passes through the lid of the retort to beneath the perforated fire-clay plate. Two such packets each containing about 5½ ozs. of sulphur are thrown in at intervals of three minutes, the opening at the upper end of the porcelain tube being closed with a plug of clay after each addition. The charcoal is renewed every seven hours, being each time heated for about an hour and three quarters before the temperature requisite for the combination with sulphur is attained. The vapour of carbon bisulphide mixed with vapour of sulphur escapes through the delivery tubes (D), passing into the first row of condensers, where it is partly condensed, together with some

sulphur, that is deposited in the solid state and is used again; from thence the uncondensed vapour passes into the second, third, etc. condensers, until at last the gas from the four retorts is conducted either through a chimney into the air, or through vessels containing a mixture of hydrated ferric oxide and calcium sulphate (*vide* 'Gas Manufacture'), by which means the sulphuretted hydrogen is retained.

Gérard in Grenelle has considerably improved the apparatus for the production of carbon bisulphide. An improved form of apparatus, as constructed by him, is shown in fig. 84.

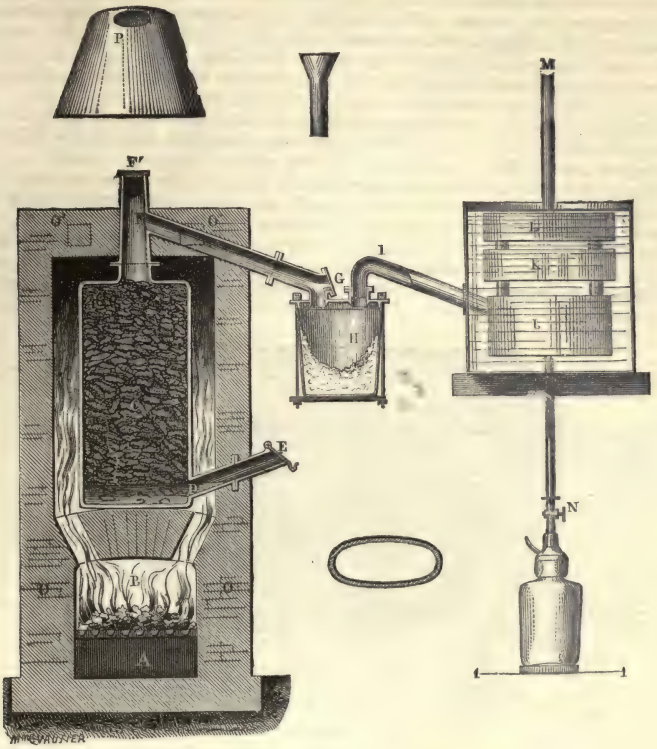


FIG. 84.

The vessel (C) in which the charcoal is heated is made of cast iron, having sides $1\frac{3}{4}$ inches thick and, as shown sectionally in the centre, is elliptical in form; it has a diameter of 4 feet 8 inches, and is $6\frac{1}{2}$ feet high. It stands upon a brickwork arch, and is heated from B by the flame which entirely surrounds it. Near the bottom is a pipe (D), fitted with a valve (E), through which the sulphur is thrown in. F is a tube of cast iron, having a somewhat conical shape toward its upper extremity, which can be closed with a lid. It is connected by means of a metal tube, furnished with a tubulus (G) which can be closed, with the receiver (H), from which the vapour passes through the tube (I) into the condensers (J, K, L), which are connected with one another by means of two tubes. To the uppermost condenser is attached a delivery pipe (M), through which the uncondensed gas and vapour escape. The whole of the condensed carbon bisulphide collects in the lowest vessel (J), that portion which condenses in K and L flowing down into J through the communicating tubes, and it is drawn off by means of the cock (N). The three cylindrical condensers (J, K, and L) are contained in a large tank 5 feet high and 5 feet wide, filled with cold water, which can be renewed at pleasure.

The cast-iron vessel (C) is charged with dry wood charcoal broken into small pieces, which are thrown in through a funnel (fig. 84), and it is then heated to bright redness. Sulphur is next thrown in at intervals at E, and upon coming into contact with the red-hot vessel, melts, is converted into vapour, and passing over the red-hot

charcoal, forms with it carbon bisulphide. As was the case with the other forms of apparatus, so also here sulphur vapour is carried over with the carbon bisulphide, and is condensed in the vessel (H), from which the sulphur can be easily removed, the more volatile carbon bisulphide passing through the pipe (I) into the condensers (J, K, L).

The addition of sulphur is carried on ten hours daily; in portions of about 3 lbs. at intervals of three minutes. The oven is heated during the night in order to completely volatilise all the sulphur; the residue of charcoal left the next morning is allowed to remain, and a new charge is added to it. For the purpose of recharging, the communication between the developing vessel and H is broken, by opening the tubulus (G) and stuffing it with a piece of moist rag. The vessel (C) is then recharged with fresh charcoal, the vapours of carbon bisulphide which are always thereby formed escaping through the chimney (F). The receiver (H) is emptied, connected again with C, G is closed, and the charcoal again heated to redness.

This apparatus yields in twenty-four hours about 44 gallons, or 570 lbs. of carbon bisulphide, which requires theoretically 480 lbs. of sulphur and 90 lbs. of carbon, but in practice 530 lbs. of sulphur and 242 lbs. of wood charcoal are used.

Gérard has recently found it expedient to surround the cast-iron vessels with brickwork, which renders them more durable and capable of lasting two or three months, whereas before they only lasted a fortnight at the most.

In fig. 85 is given a horizontal section of the new arrangement as adopted by Gérard. A is the cast-iron vessel in which the charcoal is heated, bent twice inwards, in order to increase the radiating surface; B brickwork covering; C fire-place, in which the flame circulates; and O the brickwork of the entire furnace.

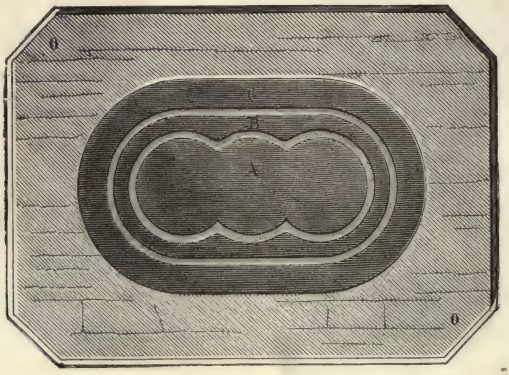


FIG. 85.

PURIFICATION OF CRUDE CARBON BISULPHIDE.—The purification of crude carbon bisulphide which contains considerable quantities of sulphur may be effected by distillation. The distilling vessel (B, fig. 86) made of sheet zinc, is fitted into a water bath (A), which is slightly heated, the vapours of carbon bisulphide passing through a wide tube (C) into a serpentine pipe (B) surrounded by cold water, where they condense; the liquid carbon bisulphide free from sulphur trickling into a vessel placed beneath E' to receive it.

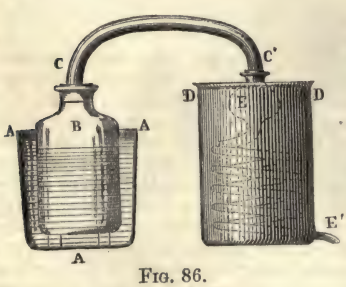


FIG. 86.

Deiss rectifies carbon bisulphide from large boilers with a flat bottom, which are 10 feet in length, 6½ feet in diameter, and 3¼ feet high. The covers are domed, and protected externally by a bad conductor of heat, in order that as little carbon bisulphide as possible may be condensed and returned to the boiler. The boiler is capable of receiving 5 tons of crude carbon bisulphide at a single charge. A man-hole is constructed at the upper part of the boiler, and also six delivery tubes which terminate in six vertically placed condensers. At the bottom of the boiler there are two serpentine pipes, through which steam can be passed. Steam being passed through one of

these pipes, the crude carbon bisulphide is heated to its boiling point (48°). The distillation of 5 tons lasts three or four days; the latent heat of 100 parts of steam sufficing to heat to its boiling point 650 parts of carbon bisulphide. The products of the different stages of distillation are separately collected, by which means carbon bisulphide is obtained of different degrees of purity, and serving different purposes. The first portions which pass over contain the easily volatile, and especially the odoriferous constituents, such as sulphuretted hydrogen, etc. The middle portions are the purest, while the last portions are impure from containing sulphur. For the purpose of distilling off the very last portions of carbon bisulphide, steam is passed through the second pipe, direct into the boiler, by which means the remainder of the carbon bisulphide mixed with steam passes over into the condensers, where both condense, the carbon bisulphide forming a layer at the bottom of the water.

When the operation is over, a workman enters the boiler, which has been previously ventilated, through the manhole, and removes the sulphur residues.

This apparatus has essentially the same arrangement as that employed in the extraction of oils, which is represented by figs. 90 and 91.

For the removal of the sulphuretted hydrogen, a small quantity of caustic soda is thrown into the boiler, which retains the sulphuretted hydrogen by combining with it.

In Bonière's apparatus the carbon bisulphide is run from a large reservoir into a still containing concentrated caustic soda, and heated externally by steam; the vapour is then made to pass through several other vessels of the same kind, some containing alkaline liquids, and some containing solutions of salts of iron, lead, or copper; from which it is distilled, and finally condensed in a condenser furnished with a serpentine tube.

Millon patented a process in which the carbon bisulphide is mixed with half its volume of milk of lime, and then carefully distilled off.

Carbon bisulphide thus obtained and purified by rectification, comes into the market in sheet-iron drums, which have a form represented by fig. 87. The plates forming the top and bottom are bent inwards, and the upper one has an opening closed by means of a screw.



Fig. 87.

Method of Storing.—In the manufacture, storing, and use of carbon bisulphide, great precaution is necessary, owing to the fact that at the ordinary temperature, so much carbon bisulphide may volatilise as to render the air in the vicinity irrespirable. Further (as has already been mentioned) the vapour of carbon bisulphide, mixed with atmospheric air in certain proportions, forms an explosive mixture, which is the more dangerous owing to the products of such an explosion being three irrespirable gases, viz., carbonic dioxide, sulphurous oxide, and the unburnt residue of the air itself, nitrogen.

Rooms in which carbon bisulphide is stored, or in which it is used, ought therefore to be isolated from other buildings and well ventilated. The vessels in which the substance is stored must be tolerably large, and so placed that they are not likely to receive a blow, or get thrown over.

Fig. 88 represents a vessel for storing carbon bisulphide, as introduced by Gérard. It is made of sheet zinc of a cylindrical shape, holding as much as 20 or 30 gallons. Receivers of the kind, to the number of 10, 20, 30, or more, are placed upon a wooden platform raised three feet from the ground. Each receiver has a cylindrical cavity at the bottom in which a tube (B B) terminates. This tube has a rim above turned outwards, which serves to secure it firmly upon the cover of the reservoir. The reservoirs are filled by fitting a funnel into the mouth of the tube (B B), and pouring carbon bisulphide through it into the reservoir; the air in the reservoir escaping through the open cock (C). When sufficient carbon bisulphide has been poured into the reservoirs, a small quantity of water is poured in to prevent the evaporation of the carbon bisulphide, the cock (C) is closed and the mouth of the tube (B) is plugged up.

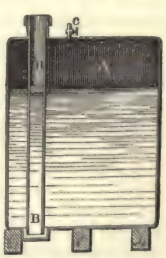


Fig. 88.

When required for use, the carbon bisulphide is drawn off from such reservoirs by means of a syphon (fig. 89), which is plunged in the tube (B′); the cock (F) is opened and carbon bisulphide to the required amount is drawn off into a vessel held beneath it. A single syphon serves for the entire number of reservoirs.

Uses.—The low price of carbon bisulphide has rendered it possible to make use of it for a number of purposes.

Thus it has been recently used for the extraction of fatty oils from oil seeds and pressed residues from which no more oil can be pressed out, and also in the extraction from crude wool of fat, which was formerly lost. The chief use of carbon bisulphide is, however, in the preparation of vulcanised caoutchouc. Carbon bisulphide is further used for purifying paraffin, for the extraction of sulphur from its ore, for the preparation of a caoutchouc solution and cement, and for filling prisms, for which purpose it is used on account of its refractive properties; it is also used as a poison for vermin, in the manufacture of aluminum, various colours, ammonium sulphocyanide, and other preparations, for dissolving phosphorus in electro-plating, etc.

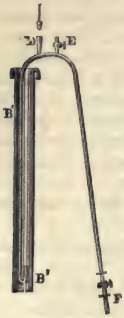


FIG. 89.

Finally, it may be mentioned that attempts have been made to replace the water in steam boilers by carbon bisulphide, since it does not require so much heat for its conversion into vapour as water does.

EXTRACTION OF FAT, OIL, ETC.—Deiss first employed carbon bisulphide for extracting fatty oils from seeds, oil cakes, and other pressed residues, and its application for such purposes has since attained considerable dimensions.

The arrangement of Deiss' apparatus is represented by figs. 90 and 91. A is a cemented brickwork reservoir, with a manhole, which is generally kept closed. The tail pipe (J)

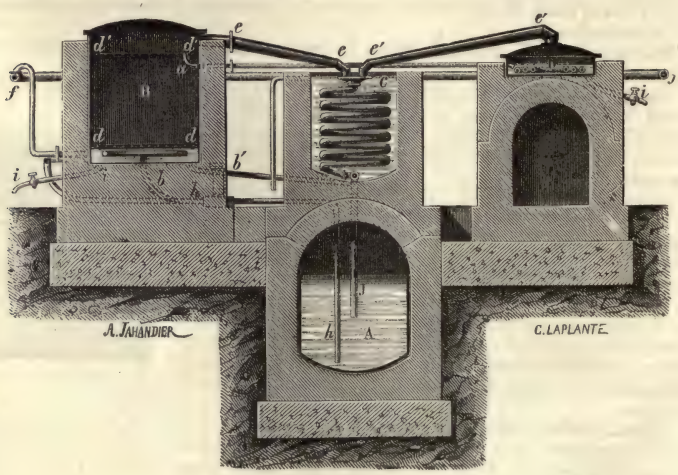


FIG. 90.

of the condenser, and the supply pipe (*h'*) of the pump (*h h*), dip into this reservoir, which is about 22 feet long, 6 feet in diameter, and nearly 6 feet deep, and lined with lead up to the height at which it is filled with carbon bisulphide and water.

The reservoir and condensers are made of iron; but since it often happens that acid residues from stearic acid manufactories have to be treated, the bottom and side walls of the extracting apparatus are made of lead, the lid only being made of iron.

The extracting apparatus (B) has a domed cover tightly screwed upon the flange of the extractor, has a capacity of 4400 gallons, and may be charged with 12 tons of oil cake. At a height of 6 inches from the floor is a perforated shelf (*d d*) which can be removed at pleasure. In the space between the bottom and this perforated shelf is a perforated coil of pipe, through which steam can be passed. At the upper part of the extractor there is a second moveable perforated shelf (*d' d'*), having above it, at the side, two pipes, which place the extractor in direct communication with the distilling vessel (D) and allow the carbon bisulphide saturated with oil to flow into the still (D) as soon as it rises to the level of the upper shelf.

Just below the lid of the extracting vessel, on a level with one another, are nine tubes (*e e*), 8 inches diameter at the extremity nearest the extractor, and 6 inches diameter at the other extremity, through which the vapour is conducted into the condenser (*c*). At each end of the extractor, between the bottom and the perforated shelf, is a tube

connected with the pump (*h h*), through which carbon bisulphide is pumped up from the reservoir (A) into the extractor. At the bottom of the extractor there is also a tube (*b b'*) which upon the opening of a cock serves to let out the entire liquid contents into the reservoir (A). Two other tubes placed at the ends, and at the bottom of the extractor, give exit to the water used in washing or steaming the apparatus. Parallel

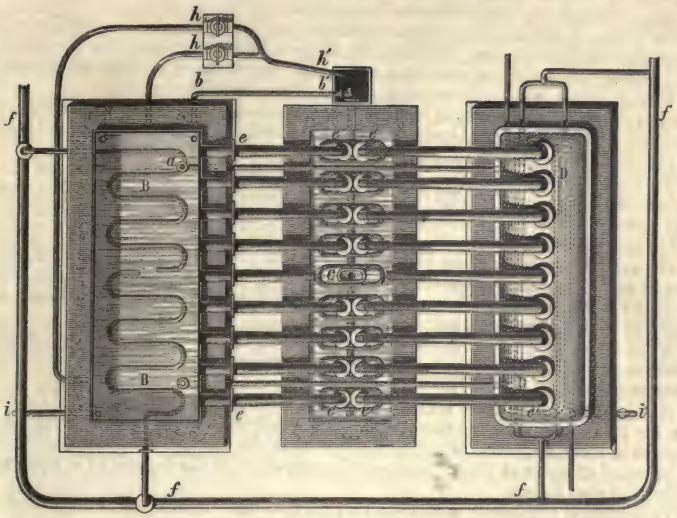


FIG. 91.

with the extractor (B) is a large distilling vessel (D) about 11 feet long, 5 feet wide, and, without the arching of the roof, 15 inches deep, holding, when half filled, about 400 gallons. During the entire course of the operation this distilling vessel is supplied, by means of two pipes, with carbon bisulphide, that flows over above the level of the upper shelf in the extractor (B), after having macerated its contents. The vapour from this still passes through 9 tubes (*e' e'*) into the condenser (*c*), and by this means the whole of the carbon bisulphide volatilised in the apparatus is condensed and collected into the reservoir (A), from whence it can be again pumped up into the extractor (B). In order to lessen the evaporation of carbon bisulphide in the reservoirs (A) it is covered with a small quantity of water.

The liquid in the still (D) is heated by means of steam supplied through the pipe (*f*) to two pipes coiled several times upon the bottom of the still, the condensed steam flowing back again into the boiler. By means of two other pipes, steam may be admitted directly into the still.

In working this apparatus, the first thing to be done is to remove the lid of the extractor (B), and fill the space between the shelves (*d d*) and (*d' d'*) with the material to be operated upon. The lid of the extractor is then fastened down, and carbon bisulphide forced into the extractor (B) by means of the pumps (*h h*). As the bisulphide penetrates the mass it becomes specifically lighter, owing to the fact that the oil with which it mixes has a specific gravity of about 0·900, while carbon bisulphide has a specific gravity of 1·293. From the macerating vessel, the liquid containing extracted oil flows in a continual stream into the distilling vessel, which is heated by the steam pipe at its bottom, and the carbon bisulphide is distilled off through the pipes (*e' e'*) and the condenser into the reservoir (A). In order to deprive the oil of the last traces of carbon bisulphide, when the extracting operation is over, steam is passed directly into the vessel (D), through the other pipes at its bottom, which are perforated, and this is continued until all the carbon bisulphide has been carried away by the steam.

The point of exhaustion of the material in the extractor is ascertained either from the duration of the filtration, or by watching the colour of the carbon bisulphide through a glass tube let into each of the pipes conducting the liquid from the extractor into the still. Although the oil is of itself colourless, there are still sufficient colouring substances dissolved out by the carbon bisulphide to admit of an opinion being formed as to whether the extracting process is complete or not; as soon as the carbon bisul-

phide passes over colourless, the extraction is considered to be complete. The cock *b* is then opened, and the liquid contents of the extractor (B) run into the reservoir.

After this operation is over, superheated steam is passed into the extractor from the perforated serpentine pipe at the bottom, and thus the whole mass is soon brought up to 100° C., any adhering carbon bisulphide being thus volatilised, and passing with the steam through the condenser into the reservoir.

The filling of the macerating vessel with carbon bisulphide takes eight hours, the maceration itself four hours; the emptying of the macerating vessel into the reservoir at the end of the operation takes two hours, and the steaming of the oil in order to free it from carbon bisulphide requires from eight to twelve hours.

After the exhausted material has been sufficiently steamed, a cock at the bottom of the vessel is opened, the condensed water is let out, the lid and upper shelf removed, and the residues spread out in the air to dry.

Working with an apparatus of the above dimensions, about 2½ tons of oil can be obtained in thirty hours from 25 tons of olive oil cake. The residues from the macerating vessel are used in Pisa for heating the boiler, which produces the steam for the whole apparatus.

The extraction of fat from bones is at present generally carried out by boiling them in closed vessels with water, an operation by which a good deal of fat is still left in the bones; its extraction may be effected with greater advantage and more completely by means of carbon bisulphide.

When bones are treated in the apparatus, a temperature of 140° C. is necessary for extraction, and this is attained by passing hot water or steam into the digester through a serpentine tube.

Bones exhausted of their fat by maceration with carbon bisulphide are very suitable for preparing bone charcoal, while on the other hand they are not fit for the purposes of the glue boiler, owing to the fact that the action of carbon bisulphide in the presence of water at 100° C. causes a decomposition of the organic substance, which renders the glue brittle.

This effect is apparently similar to that exerted upon wool when it is treated with carbon bisulphide for purposes of extracting its fat in the above manner.

Extraction of Fat from Wool.—The apparatus used for this purpose by Moison and Jérome is represented by fig. 92. The extractor consists of a large cylindrical

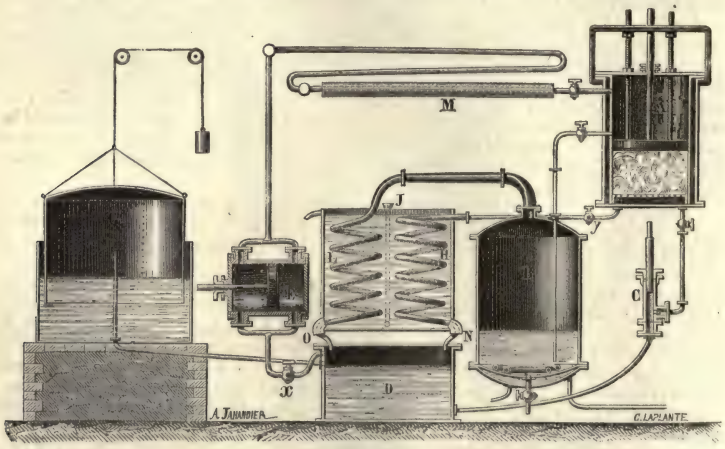


FIG. 92.

vessel (A) of sheet iron, with a close-fitting cover and double walls, between which hot water circulates. At a short distance from the bottom there is a perforated shelf upon which the wool to be extracted is placed. A perforated plate can be pressed down upon the wool by means of screws. A pump (C) forces the carbon bisulphide from the reservoir (D) into the cylinder (A) beneath the perforated shelf, and a pipe placed as near as possible to the centre of the extractor conducts the fat dissolved out by the carbon bisulphide into the still (B), which is heated by a coil of pipe at the bottom, and has a cock for the purpose of letting out the fat freed from carbon bisulphide. By a second coil of perforated pipe superheated steam can be passed directly into the fat, so as to remove the last portions of carbon bisulphide.

A worm tube (L) placed in the vessel (J) condenses the vapour of carbon bisulphide escaping from the still (B) and delivers it into the reservoir (D). By means of the air pump (E) air is pumped out of the reservoir (D) and pressed into the extractor (A), through a tube several times bent and fitted towards the end with a jacket (M) through which water is passed at a temperature of 70° C. The heated air being at the end of the operation forced through the wool, carries with it the last portion of carbon bisulphide, through a pipe at the bottom of the macerating vessel into the condenser (H), where the vapour is condensed and flows into the general reservoir (D). The entire apparatus is in communication with the interior of a gasometer (*g*), which serves to regulate the pressure in the interior of the apparatus in such a way that it is always the same as the pressure outside. In the tube leading from the macerating vessel (A) into the distilling vessel (B), as well as at the ends (O and N) of the condensing worms, pieces of glass are let in, which serve to show the colour of the liquid flowing from A to B, and also the rapidity of the distillation. Close to each of these glass windows is a small cock, from which a small quantity of liquid may be drawn off to test whether the extracting process is still going on or not; for which purpose a little of the liquid is placed upon a watch glass, and allowed to evaporate in order to see if a residue of fat remains.

The cock (X) between the reservoir (D) and the air pump (E), and the cock (Y) between the macerating vessel (A) and the condensing worm (H), have a double perforation, so as to admit of these parts of the apparatus being, at pleasure, either placed in communication with one another, or of air being drawn in by means of the air pump (E) through the cock (X), forced through the apparatus, and expelled by the cock (Y).

The macerating vessel (A) is charged with about 10 tons of wool, and the press plate screwed down so as to reduce its bulk to at least one half. The pump (C) is then set going and the macerator gradually filled with carbon bisulphide, which enters underneath the perforated false bottom, penetrates the wool gradually from below upwards, passes through the holes of the press plate, and flows at last into the distilling vessel (B). The filtration of the carbon bisulphide through the wool is continued until the liquid flowing from A to B, when examined through the glass window, appears colourless, and a portion of it drawn off and allowed to evaporate leaves no residue of fat.

In proportion as the carbon bisulphide containing dissolved fat flows into the distilling vessel, it is evaporated by means of the serpentine tube at the bottom, the vapour condensing in the worm (L). When the extracting process is complete, the cock connecting the pump (C) with the macerator (A) is closed, and the air pump (E) set in motion. By this means the air is drawn from the extractor (A) through the tube containing the cock (Y), the greater portion of the carbon bisulphide adhering to the wool being carried with it at the first few strokes of the pump, through the condenser (H) into the reservoir (D). When no more liquid is observed to flow past the glass window (N), water at a temperature of 70° C. is allowed to circulate in the jacket (M); the air thus warmed penetrates the wool, removing the greater part of the adherent carbon bisulphide as vapour which is condensed in the worm (H). At the end of the process the cocks (X) and (Y) are set so that air can enter through the former and, after having passed through the wool, escape through the latter; it always contains traces of carbon bisulphide and is therefore conducted into the open air. The wool thus deprived of fat and dried, is taken out and freed mechanically from particles of dust.

By this method, a considerable amount of fatty substance is obtained from sheep's wool, and it may be employed advantageously in the preparation of soap.

The materials treated with carbon bisulphide in order to obtain the fatty ingredients they contain are:

I. The dark-coloured tar-like residues of stearic acid manufactories, which are products of the treatment with sulphuric acid. They yield to carbon bisulphide from 18 to 20 per cent. of fatty acid, which was almost entirely lost before. The residues are mixed with sawdust in order to facilitate the filtration of the dissolved portion.

II. The dark brown cart grease which oozes from the axles of cart and carriage wheels, becoming hard. For obtaining the fatty acids from this kind of refuse, it is first of all treated with sulphuric acid, washed, and dried.

III. Tow and rags used in cleaning and oiling machinery. These can be treated at once with carbon bisulphide without the addition of sawdust. This treatment of rags, etc., has a threefold advantage: recovery of fat or fatty acids; purification of the rags so that they can be used again; and the prevention of danger arising from the liability to spontaneous ignition which oily rags or other greasy materials possess when piled together in heaps.

IV. The refuse of the preparation of bees' wax, which yields with carbon bisulphide a certain amount of yellow wax that is useful for many purposes.

V. Sawdust that has been used for filtering oils after purification with sulphuric acid.

VI. The dirty sediment produced by the treatment of various oils with sulphuric acid contains about 50 per cent. of oil, which may be extracted with carbon bisulphide, after treating the sediment with boiling water, to destroy the sulpho-fatty acids, drying, and mixing it with sawdust.

VII. Bones from slaughter-houses and kitchens, that are to be used in the preparation of bone black, yield with carbon bisulphide from 10 to 12 per cent. of fat.

VIII. The expressed residues of oil seeds, such as rape, sesame, nettle, flax, etc., when they cannot be profitably employed as fodder. In all cases it is necessary to break up the oil cakes into small pieces before treating them with carbon bisulphide, so as to insure thorough penetration of this substance. The residue left after extracting the fat is hardly suitable for fodder, but it is a valuable manure.

IX. The cracklings, or greaves, obtained by the melting of tallow.

X. The pressed cacao beans, from which no further cacao butter can be obtained by mere pressing.

XI. The pressed residues obtained in the preparation of olive oil; there are two sorts, according to the way in which the expressing operation has been performed. Sanza is the residue obtained by simply crushing and pressing the olive. It contains, besides the pulp of the flesh, also the kernels, which increase the weight and volume of the mass very considerably, without being of any intrinsic value. Buccia is prepared from sanza by boiling it for a short time with water, until the kernels are detached, and fall to the bottom of the pan; while the flesh of the fruit remains suspended in the liquid. This is skimmed off, placed on a sieve, and pressed. Although a small quantity of oil is thus pressed out with the water, the buccia or doubly pressed residue contains a larger amount of oil than sanza, because the kernels have been removed. This rich oily residue is used in Italy as fuel, and especially in cases of festivity, on account of the bright flame yielded by it. On this account its price is so high, that although it contains from 22 to 25 per cent. of oil—that from Calabria, indeed, often containing 28 per cent.—there is difficulty in obtaining a sufficient quantity at a price cheap enough to render its working up practicable.

SELENIUM AND TELLURIUM.

Se	Symbol	Te.
79·5	Atomic Weight	128.

These two rare elementary substances are closely analogous to sulphur in their chemical relations. Selenium occurs naturally either with sulphur or combined with other elementary substances as selenides, which resemble sulphides and are often present in small proportions in some kinds of pyrites; hence selenium is frequently found in the flue dust deposited in the chambers of sulphuric acid works where pyrites is burnt as a source of sulphur. A mineral occurring in the Harz mountains and consisting of lead, selenide, and cupric selenide, is one of the chief sources of selenium. Tellurium occurs naturally in the free state and in combination chiefly with bismuth as tetradymite, also with gold, silver and lead; combined with oxygen, it occurs as tellurite.

Selenium is a solid substance of a brown colour and considerable lustre; it is, like sulphur, capable of assuming two allotropic conditions, one of which has a vitreous texture and a specific gravity of 4·3; the other is crystalline, has a specific gravity of 4·8, melts at 217° and is volatilisable.

Tellurium is a crystalline brittle substance of a white metallic colour, very considerable lustre, and decided metallic characters. Its specific gravity is about 6·2, it melts at about 500°, and is volatilisable at a higher temperature.

The compounds of selenium and of tellurium closely resemble in constitution the compounds of sulphur as shown by the formulæ of the compounds corresponding to sulphuretted hydrogen, sulphurous acid, and sulphuric acid.

Hydrides	H_2S	H_2Se	H_2Te
Acids	H_2SO_3	H_2SeO_3 (Selenous Acid)	H_2TeO_3 (Tellurous Acid).
	H_2SO_4	H_2SeO_4 (Selenic Acid)	H_2TeO_4 (Telluric Acid).

The general characters of the corresponding compounds also approximate.

The selenates are frequently isomorphous with and otherwise resemble the corresponding sulphates, but the tellurates as well as the tellurites present more the characters of salts containing an acid oxide of a metal.

PHOSPHORUS.

SYMBOL P. ATOMIC WEIGHT 31.

History.—This substance was discovered in 1669, by Brandt of Hamburg, and shortly afterwards by Kunkel, but it is probable that he was in some way aware of Brandt's method of preparation, which consisted in distilling the residue from the evaporation of urine with charcoal. In 1743 Marggraf prepared phosphorus from other substances, such as mustard seed, garden cress seeds, wheat, etc.

Many opinions were formed as to the chemical constitution of phosphorus. According to Stahl, it was a compound of phlogiston and hydrochloric acid. Boerhave considered it to be a compound of phlogiston and sulphuric acid. The former view was the one most generally adopted, until it was proved to be incorrect by Marggraf, who considered phosphorus to be a combination of phlogiston and phosphoric acid. Lavoisier showed however, that when phosphorus is burnt it combines with oxygen, being thus converted into phosphoric acid, and that phosphorus ought therefore to be considered as a constituent of phosphoric acid.

Occurrence.—Owing to the readiness with which phosphorus combines with oxygen, it does not occur naturally in the free condition; but it occurs abundantly in combination with oxygen and metallic bases as phosphates. Thus calcium phosphate occurs as a mineral called apatite (a compound of calcium phosphate with calcium chloride and fluoride) and as osteolite; aluminum phosphate as wavellite; ferrous and ferric phosphates as green iron-stone; lead phosphate as pyromorphite. Sombrerite, a mineral found in the Antilles, under guano beds, probably is limestone partly converted into calcium phosphate by the action of solution of guano salts; it contains about 65 per cent. calcium phosphate and 17 per cent. aluminum phosphate. Large quantities of calcium phosphate also occur in guano, the excrementitious deposit of sea birds, which sometimes contains from 75–80 per cent. A guano which is imported from Navassa in North America, and is related to sombrerite in composition, contains 30 per cent. of calcium phosphate. Coprolites are also rich in calcium phosphate.

Phosphorus is also very widely distributed in the vegetable kingdom, where it is chiefly found as phosphates. Seeds are especially rich in phosphates; thus the ash of wheat contains from 39–47 per cent. of phosphates; that of peas and beans about 40 per cent.; maize ash contains about 50 per cent. Other parts of plants are less rich in phosphates, the ash of maize and pea straw containing only 12–15 per cent.; that of hay, clover, bean straw, etc., from 7–8 per cent. only.

Phosphorus is also abundant in the state of phosphates in the animal kingdom, where it occurs chiefly in the bones, which contain from 25 to 27 per cent. of phosphoric acid. A still greater percentage of phosphorus is found in the teeth and their enamel. The other organs of animals also contain more or less phosphorus.

Characters.—There are two modifications of phosphorus; the ordinary crystallisable phosphorus, and the red or amorphous phosphorus. Ordinary phosphorus is colourless, or of a slightly yellow tinge, and is often quite transparent; it has an unpleasant smell and taste. At a moderately warm temperature it has a waxy consistency, and may be easily cut; but at lower temperatures phosphorus is hard and brittle; a small admixture ($\frac{1}{500}$) of sulphur has the same effect. Phosphorus melts at 44°, forming a thick oily liquid that may be cooled much below the melting point without solidifying; it boils at 290°, and the vapour has a density of 62, as compared with hydrogen, even when heated above 1000°. When heated above its melting point, phosphorus takes fire in the air, and at the ordinary temperature it gradually oxidises, giving off a faint light. This phenomenon is termed phosphorescence. Even at the ordinary temperature this process of oxidation is apt to cause sufficient heating of the phosphorus to make it melt and burn, and on this account phosphorus must be kept under water out of contact with the air. Phosphorus has a specific gravity of 1·826–1·840. It is insoluble in water, and almost insoluble in alcohol; slightly

soluble in ether, volatile, and fat oils; but very readily soluble in sulphur chloride and carbon bisuphide.

When phosphorus is allowed to oxidise slowly in contact with a limited amount of air, the product of oxidation consists of the trioxide or phosphorous oxide only (P_2O_3), but when the oxidation is more rapid, pentoxide or phosphoric oxide (P_2O_5) is formed. It is remarkable that phosphorus scarcely emits any light in an atmosphere of pure oxygen, but upon rarefying the gas, or diluting it with another gas that itself exerts no action upon phosphorus, the phosphorescence increases in proportion to such dilution. Phosphorus which is only partly covered with water induces oxidation of atmospheric nitrogen and the formation of dense vapours of ammonium nitrite, ozone being produced at the same time.

Phosphorus, even when entirely protected by water, undergoes a change in direct sunlight, passing into the amorphous condition. The clear transparent sticks of phosphorus become gradually less transparent, the change beginning at the surface and gradually penetrating the entire mass. For this reason phosphorus requires not only to be kept under water, but also to be protected from sunlight.

Phosphorus abstracts oxygen from a number of substances, such as nitric acid, chromic acid, chloric acid, etc., which are either thus reduced to lower oxides, or entirely decomposed.

Phosphorus combines readily with chlorine, bromine, iodine, and sulphur. It does not combine directly with hydrogen; but upon heating phosphorus with concentrated solutions of the caustic alkalies, phosphoretted hydrogen is formed.

Amorphous phosphorus has been long known; it was however for some time considered to be a lower oxide of phosphorus, until, in 1848, Schrötter proved it to be an allotropic modification of phosphorus. When ordinary phosphorus is exposed under water to the action of sunlight, an opaque reddish crust is formed upon its surface, which increases in depth until the crust formed is so thick that the sun's rays can no longer penetrate through it. This change consists in the conversion of ordinary or crystallisable phosphorus into the amorphous or allotropic form. The change may be effected with greater rapidity by heating phosphorus in an atmosphere free from oxygen to a temperature of 160°, either alone, or in the presence of a small quantity of iodine, which accelerates the alteration.

Amorphous phosphorus has a brownish red colour; it is odourless, opaque, hard and friable. It has a specific gravity of 2·106, the spec. grav. of ordinary phosphorus being 1·826–1·840. Amorphous phosphorus begins to burn at a temperature of 200°; exposed to the light, however, it takes fire at a temperature of 55°–60°. It undergoes no change when exposed to the atmosphere, and is insoluble in all those mixtures which dissolve ordinary phosphorus, such as alcohol, ether, fat oils, carbon bisulphide, etc. Owing to its not being poisonous, and to its taking fire when rubbed with potassium chlorate, amorphous phosphorus is used in the manufacture of matches.

Preparation.—The raw material used in the manufacture of phosphorus is bone ash, obtained by removing the cartilaginous tissue from bones by burning them. Bone ash varies somewhat in composition, the amount of calcium phosphate generally varying between 82·5 and 84·5 per cent. Besides this, it contains from 2 to 3 per cent. of magnesium phosphate, from 8 to 10 per cent. of calcium carbonate, and 3 to 4 per cent. of calcium fluoride.

The calcined bone ash is decomposed with sulphuric acid, and thus the insoluble neutral tricalcium phosphate is converted into the soluble acid calcium phosphate, according to the equation:

$$Ca_3P_2O_8 + 2H_2SO_4 = CaH_4P_2O_8 + 2Ca\,SO_4.$$

After separating the calcium sulphate, the clear solution is evaporated nearly to dryness, the residual acid calcium phosphate intimately mixed with charcoal and dried, so as to deprive it of water and form calcium metaphosphate:

$$CaH_4P_2O_8 = CaP_2O_6 + 2H_2O.$$

The mixture is then heated to redness, and a part of the calcium metaphosphate is reduced and phosphorus liberated, as shown by the following equation:

$$\underset{\text{Calcium metaphosphate}}{3CaP_2O_6} + 10C = \underset{\text{Tricalcic phosphate}}{Ca_3P_2O_8} + 10CO + 4P.$$

Calcination of the Bones.—This operation has for its object the destruction of the organic substance of the bones, and it is generally carried out in kilns similar to those used in lime burning.

Fig. 93 represents a kiln of the kind, which is so constructed that the escaping gases are burnt, and thus nuisance is avoided. A is a cylindrical shaft furnace, the mouth (A′) of which is contracted and closed by a lid of cast iron. By means of lateral

apertures (B) opening into a circular flue extending entirely round the body of the kiln, the lower part of it near the furnace communicates with the chimney (D D). The bars of the grate (C) are moveable, and are supported upon cross bars. To set the operation going, the door (E) is opened, and the fire bars laid in and covered with some easily combustible material, which is set fire to. As soon as the fire burns brightly, the door (E) is closed and a fire of shavings made at (D'), in the chimney (D), so as to draw out and burn the gas escaping from the fire-grate (C), through the side openings (B), and upon closing the door (D') through the chimney (D D) into the air. When the oven has been heated in this way, bones are thrown in through the mouth (A') until the kiln is full; then A is closed for a moment and the fire bars are drawn out, so that the burnt bones fall down upon the lowest part of the kiln, whence they are drawn out through the opening (B). Directly the burnt bones have been drawn out, this opening is closed and more bones are thrown in at A'. The kiln is thus kept in constant operation, the organic substance of the bones sufficing for the calcination after combustion has been once started.

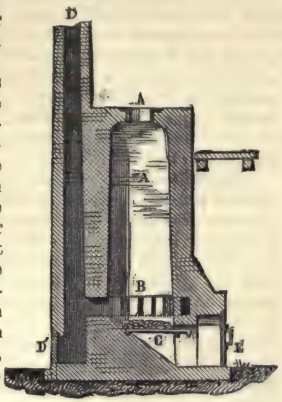


FIG. 93.

Fleck's furnace consists of a shaft which is charged through a lateral opening above, the combustion being started by some easily combustible fuel. The products of combustion escape through the highest part of the shaft into a horizontal flue, at the mouth of which a fire is kept up through which the noxious gases pass and are burnt, the heat evolved being used for evaporation. The horizontal flue terminates in a chimney. The yield of calcined bone ash obtained in this operation amounts to from 50 to 55 per cent. of the weight of the bones employed.

Crushing the burnt Bones.—The extent to which the crushing of the bones is carried varies. In some places the bones are reduced to powder, and sometimes only to pieces about the size of peas. The crushing of the bones to pieces of the size of lentils is the most suitable for further working. The crushing operation is effected either between rollers or stampers.

Treatment with acid.—The quantity of sulphuric acid required for the decomposition of the bones depends upon its concentration. 100 parts of bone ash require for decomposition 66 parts by weight of concentrated sulphuric acid, or 100 parts of acid of sp. gr. 1·49.

According to other authorities—

100 parts of bone-ash require			106·73	parts of sulphuric acid,		sp. gr.	1·490.
„	„	„	85·68	„	„	„	1·652.
„	„	„	73·63	„	„	„	1·747.

The decomposition of the bone ash by sulphuric acid is carried out in tubs lined with lead, in which 100 parts by weight of boiling water is mixed with 20 parts of sulphuric acid of sp. gr. 1·490; into this mixture is then thrown, in small quantities at a time, 20 parts of bone ash powder. A lively frothing takes place, owing to the evolution of carbonic acid. As soon as this has ceased, further quantities of boiling water, sulphuric acid, and bone ash are added, this being repeated until four separate charges have been thrown into the tub, making in all 80 parts of bone ash and 80 parts of sulphuric acid of sp. gr. 1·490. The mass is kept warm for twenty-four hours, during which time it is often stirred, and is then left at rest for ten hours. The clear liquid is then drawn off from the precipitate through a leaden pipe into a wooden gutter lined with lead, then passed first through a filter, and afterwards into leaden evaporating pans. The precipitate which remains in the tubs is covered with a quantity of water equal to that originally used, stirred up and left to settle. The clear liquid is then drawn off and used to wash the residues of four or five other tubs. In this way the liquid of the fifth or sixth tub is brought up to a concentration represented by sp. gr. 1·070 to 1·085. The last portions of wash water are used for preparing fresh liquors.

This kind of washing is sometimes replaced by a process of filtration. For this purpose the residues are placed in a tub with a double bottom. The residues are laid upon the upper perforated bottom of the tub, which is covered with a cloth, and are washed out by pouring water upon them. Gentele covers the perforated bottom of the vat with quartz sand, instead of with a cloth. Recently it has been proposed to use centrifugal machines for the washing.

Concentration of the Liquor.—The combined liquid is concentrated to a sp. gr. 1·188, and left to cool in large leaden vessels. It is afterwards decanted from the gypsum deposited, and filtered by passing it through a filter of sand or wool. It is next evaporated until it has a specific gravity of 1·277, left to cool and settle, and once more decanted and filtered. The filtered liquid of the last operation is then evaporated to a syrupy consistency (about sp. gr. 1·49), and mixed with dry powdered wood charcoal, in the proportion of 100 parts of syrup to 20 parts of charcoal. This mixture is dried in cast-iron pans, by heating and constantly stirring, and finally heated to low redness. The excess of sulphuric acid is thus decomposed by the charcoal, carbonic oxide, carbonic acid, and sulphurous oxide escaping, which are passed into a chimney.

Distillation of Phosphorus.—The mixture submitted to distillation consists of acid calcium phosphate, charcoal, and a small quantity of water. It is put into retorts of stoneware or fire clay, which are three fourths filled, then smeared over with clay, carefully dried, and placed in furnaces. The furnaces employed are galley furnaces (fig. 94). Each furnace holds ten retorts, which are heated by a common fire, five on each side. The hot air from the furnace passes through the flue (A) underneath the retorts, round which it plays, and finally escapes into the common flue (D). Above (D) is an evaporating pan (J), in which liquors are concentrated. The neck of each retort is connected with a copper adapter (K), terminating in the copper receiver (E). The copper adapter is luted to the neck of the retort with a luting consisting either of lime, blood, iron filings, and powdered sulphur, or of dry loam moistened with linseed

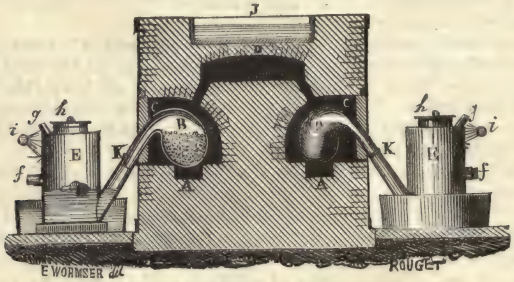


FIG. 94.

oil. The receiver (E) is furnished with a wide opening above, closed air-tight by the lid (*h*); *g* is a small tube through which air and other gases escape from the apparatus; *f* is a tube for allowing the excess of water contained in the receiver to escape in proportion as phosphorus collects in the receiver. The retorts having been charged and placed in the furnace in the above manner, the niches (C C) are bricked in, and the fire lighted. At first a fire of turf is made, care being taken to heat the retorts gradually, the temperature continually increasing for 12 hours, and finally wood is thrown into the fire, and the heat kept up so long as anything distils over or gases are seen to escape. The gases first evolved consist of air and steam; then follow hydrogen and carbonic oxide, the latter being formed by the action of wood charcoal upon the water of the acid calcium phosphate. A small quantity of sulphurous oxide is also formed. After a short time combustible gases escape, which ignite upon coming into contact with the air; these consist of phosphoretted hydrogen and carbonic oxide. This point indicates to the workman that the distillation of phosphorus has begun. In proportion as phosphorus collects in the receivers, the level of the water in them rises, and it flows out through the tube (*f*), so that the pressure does not become great enough to cause injury to the lutings of the retorts. If in course of the operation however the lutings crack, and an escape of phosphorus vapour takes place, the cracks are smeared over again carefully with luting. The heat is continued as long as inflammable vapours escape at *g*; the distillation occupying in all about 60 hours. During the distillation, especially towards the end, when less easily fusible mixtures of phosphorus and charcoal, small quantities of red phosphorus, and perhaps some silicon, pass over, a stoppage may easily take place in the adapters. In such case, a workman, whose hand is protected by a long wet leather glove, removes at intervals such solid pieces. In like manner, the first portions of phosphorus which distil over and, being inflated with gas, float on the surface of the water in the receivers, are pressed down under water with the hand. Upon the receivers becoming too hot, either cold water is poured in at *h* from a can, or the receivers are sprinkled with

water issuing in a fine jet from the pipe (*i*). The water collects in a common gutter, which conducts it away.

As soon as the distillation is over, the retorts and receivers are taken to pieces, the adapters thrown into cold water, and the raw phosphorus removed from the receivers.

Since the gas which escapes during the distillation would, if breathed, be highly injurious to the workmen, the receivers are covered with a wooden roof, connected with a ventilating chimney, by which this gas is drawn off.

Several changes have of late been made in the construction of the furnaces. A furnace similar to the one above described, which is still in use in France, holds from 24–36 retorts, in rows of 12 or 18 respectively, placed against each other, and each row is heated by a separate fire. The retorts have a globular form, and are placed horizontally. The necks of the retorts are bent slightly upwards.

In a few phosphorus works in Germany furnaces are employed which hold as many as 42 retorts. These furnaces are galley furnaces, in which the retorts are placed above one another, each side of the furnace holding 21 retorts. Each side is heated by a special fire, and both furnaces communicate above in a common flue. The retorts are made of stoneware; they have a cylindrical shape, and are prolonged so as to form a neck. The products of distillation pass into an upright copper tube, and from thence into the receivers.

The receivers have also been altered both in shape and material. At one time it was usual to employ copper receivers; these were succeeded by receivers of glass; the material now chiefly employed is earthenware. The receivers are generally made in the form of jars, and are placed in couples before each retort. Bell-shaped receivers are also employed, secured by an hydraulic joint.

A furnace may here be mentioned, constructed by Fleck, which is suitable for firing with coal or coke, all the other furnaces yet mentioned being only suitable for turf and wood. Fleck's furnace consists of arched fire chambers, separated from one another, and each heated by itself. Each of these chambers contains five cylindrical retorts placed directly over the fire. The retorts are made of fire clay, and are in communication with bell-shaped receivers. The heated air of each furnace passes through an opening in the arched roof, into a common horizontal flue, above which are placed pans for concentrating the liquors.

Fleck's method of preparing phosphorus consists in digesting one part of broken bones, which have been deprived of their fat, for 6 or 7 days, with four parts of hydrochloric acid of sp. gr. 1·048, after which time the liquor is drawn off, and the residue again treated with hydrochloric acid having a strength equal to sp. gr. 1·020. The result of this second treatment is a dilute liquor which is used in the digestion of fresh bones. The hydrochloric acid decomposes the tribasic calcium phosphate into acid calcium phosphate and calcium chloride. A liquor is thus obtained of sp. gr. 1·118, which, on account of its containing large quantities of free hydrochloric acid, is evaporated either in earthenware vessels or brickwork pans. The liquor when cooled forms a crystalline mass, which is then pressed, and mixed with one fourth its weight of powdered wood charcoal, and submitted to distillation in Fleck's furnace. There remains in the retorts, after the distillation is over, a mixture of tribasic calcium phosphate and charcoal. This residue is incinerated, treated with concentrated hydrochloric acid, and the liquor thus obtained treated for phosphorus as before.

This process possesses the advantage that glue is obtained, as a by-product, from the bones treated with hydrochloric acid.

In Gentele's process bone ash powder is macerated with hydrochloric acid, and the liquor neutralised with a solution of ammonium carbonate. There is thus formed a precipitate of tribasic calcium phosphate, and a solution of sal ammoniac, which is drawn off and treated for sal ammoniac, while the precipitate is treated with sulphuric acid and charcoal, and distilled. Ammonium carbonate is obtained by carbonising the bones, and if its amount is not sufficient, it is partly replaced by lime.

In the method of Cari-Montrand a mixture of bone ash and charcoal is placed in stoneware retorts, heated to redness, and hydrochloric acid gas passed over it. The excess of hydrochloric acid condenses together with vapour of phosphorus, water, etc., in the receivers, and the acid is used for mixing with unbroken pieces of bone and charcoal powder. For this purpose the bones are covered with the dilute hydrochloric acid, the requisite quantity of powdered charcoal is added, and the mixture obtained is dried and distilled in a current of hydrochloric acid gas. The residue in the retorts consists essentially of calcium chloride and charcoal.

In Donovan's method, lead phosphate is heated to redness with charcoal. The lead phosphate is prepared by acting upon bone ash with nitric acid, and precipitating the liquor thus obtained with sugar of lead, so that the whole of the phosphoric acid is precipitated as lead phosphate. The precipitate is separated from the liquid, thoroughly dried, mixed with charcoal, and then heated to redness.

Gerland proposes treating bone ash powder with aqueous sulphurous acid, and heating the liquor thus obtained. Tribasic calcium phosphate is precipitated and is treated for phosphorus in the ordinary way. The sulphurous oxide which escapes is condensed in a coke tower for further use.

In Claude Brison's process, calcium phosphate, silica, combustible material, and soda are melted together in a shaft furnace. The mouth of the furnace is closed, and the escaping vapour conducted through a lateral aperture into the condensing apparatus. It is necessary in this process that the draught should be strong enough to overcome the pressure of the column of water in the condensers. The furnace is recharged at intervals and the operation is, therefore, continuous. The rationale of the process is that silica liberates phosphoric acid, which is then reduced to phosphorus by the action of the charcoal furnished from the combustible material.

Purification of crude Phosphorus.—There are various methods of purifying the product obtained as above described; it generally contains some amorphous phos-

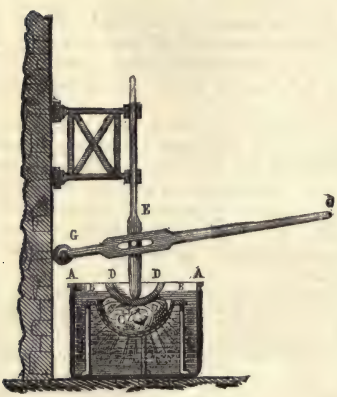


Fig. 95.

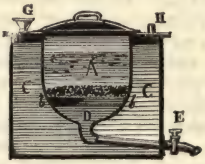


Fig. 96.

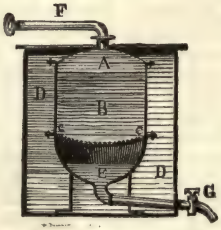


Fig. 97.

phorus, carbon, silicon, etc. The process of purifying raw phosphorus consisted formerly in throwing it into earthenware vessels containing water, and then melting it at a temperature of 60°. After it had cooled and become solid, it was bound up tightly in a sack of moist chamois leather (c, fig. 95), which was then laid upon a copper strainer standing in a vessel (A A) containing water heated to 50°. Upon the phosphorus melting, a semi-globular dish (D D) was laid upon the sack and pressed down upon it by means of the rod (E) and the lever (G G), the pressure being at first slight and gradually increased. The melted phosphorus pressed through the leather collected at the bottom of the vessel A A.

A more modern method of purifying raw phosphorus consists in passing melted phosphorus first of all through a layer of animal charcoal, and finally through a piece of chamois leather. The apparatus is shown in figs. 96 and 97. The bone charcoal is laid upon the perforated bottom (*b b*) of the vessel (A) in a layer of about 6 inches. The vessel (A) is about two thirds filled with water, the temperature of which is raised to 60° by means of the water bath (c c), and then the raw phosphorus is laid upon the layer of charcoal. The phosphorus soon begins to melt, filters through the layer of charcoal and the perforated bottom, collecting at D. Upon opening a cock (E) it flows through a tube (F, fig. 97) into a second vessel (B) filled with water, kept also by the aid of a water bath at the same temperature as the water in A. In B is also a perforated bottom (C C) covered with a piece of chamois leather, upon which the phosphorus collects. So soon as phosphorus has passed into B, the tube (F) is connected with a pump which forces warm water into A. The melted phosphorus is then pressed through the leather and collects at E, whence it is drawn off through a cock (G).

Another method consists in pressing melted phosphorus by the aid of steam through cylinders furnished with plates of porous brick. The raw phosphorus is previously mixed with powdered charcoal in order to prevent too rapid stoppage of the porous

brick plates. The charcoal powder forms a layer above the porous brick plates, and is removed and submitted to distillation in order to obtain the phosphorus retained by it.

According to R. Wagner, Messrs. Violet of Paris purify raw phosphorus in the following manner: Raw phosphorus is melted in a copper boiler and mixed with 3·5 per cent. of ordinary sulphuric acid and 3·5 per cent. of acid potassium chromate. A slight frothing takes place, and the phosphorus appears beneath the green liquid clear and colourless. It is then taken out, washed, and cast into sticks. 100 parts of raw phosphorus, thus treated, yield 96 parts of refined phosphorus.

In Germany the refining or purifying of raw phosphorus is effected by a process of distillation. The raw phosphorus is melted under water in a copper pan, and in order to prevent ignition upon pouring it out, it is mixed with 15 per cent. of sand. This mixture is then put into cast-iron retorts which are placed in a furnace, each retort being supported upon a couple of iron bars over the grate, in such a position that its neck inclines downwards, protruding from a niche in the wall of the furnace, with its mouth dipping $\frac{1}{2}$ to $\frac{3}{4}$ in. into water contained in a wooden tub placed in front of the furnace. The retorts are heated slowly in order to drive off as much adherent moisture as possible, as, upon strongly heating in presence of water, large quantities of phosphoretted hydrogen are formed. After the greater part of the water has been driven off, inflammable gas containing phosphoretted hydrogen is observed, which indicates that the distillation of phosphorus has begun. Immediately beneath the necks of the retorts are leaden dishes for collecting the phosphorus, which is removed from time to time. Since, in case of neglect on the part of the workman, explosions are apt to occur which scatter about the phosphorus in the receivers, it is advisable not to allow too great quantities of phosphorus to collect in the receivers.

Phosphorus is moulded in various ways, the most general form given to it being that of sticks.

In order to form phosphorus sticks, the plan adopted in some works is to dip glass tubes of the required aperture into melted phosphorus, which is drawn up in the tubes by sucking with the mouth, care being, however, taken that there is a layer of water between the mouth and the phosphorus. The opening of the tube is then closed with the thumb and the whole quickly dipped into cold water; the phosphorus then solidifies and contracts, and may be readily removed. Glass tubes have been of late employed in France to which an iron tube is attached furnished with a cock. The glass tube is dipped into the phosphorus, which is drawn up with the mouth, the cock then closed, and the tube immersed in cold water.

By K. Seubert's method, which has recently received much application, phosphorus is melted in a vessel (I, fig. 98) contracted below and supported in the water bath (H H). The vessel (I) terminates in a tube closed by the cock (J) and communicating with the vessel (L L), which is filled with water. A glass tube (M M) is pushed into this tube at M. Upon opening the cock the phosphorus flows into the glass tube until within 1 to $1\frac{1}{2}$ in. of the furthest end, and solidifies in it. The cock is then closed, and also the end of the glass tube, either with the stopper (N) or with the thumb.

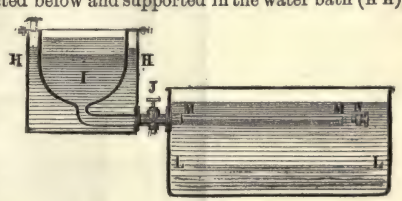


FIG. 98.

The glass tube is taken out, immersed in cold water, and the phosphorus stick removed. The tube is then again fitted into the mouth of the cock, and once more filled with phosphorus in the above manner.

Granular Phosphorus.—In order to obtain granular phosphorus, for the preparation of which Seubert's machine is available, it is only necessary to pour a layer of hot water at a temperature of 45–50° from 2 to 3 in. in height, very carefully, upon a board into the vessel (L L) containing cold water, in such a way that a mixing of the hot and cold water is prevented. The cock (J) is then opened so as to allow the phosphorus to drop, each drop solidifying immediately upon contact with the lower layer of cold water. Phosphorus in the form of very fine grains may be obtained by melting it beneath water, or better under alcohol, agitating it violently while cooling.

The proportion of refined phosphorus obtained by careful working does not exceed 8 or 10 per cent. of the bone ash employed, since, owing to breakage of retorts and combustion, some phosphorus is always lost.

Packing.—Phosphorus is packed in water in hermetically closed tin canisters, each canister holding from 5 to 6 lbs. of phosphorus. In order to test if the soldering is water-tight, the canisters are placed upon sheets of white blotting paper, a moistening

of the paper indicating an imperfection in the soldering. The canisters are then packed in barrels or boxes. In order to prevent bursting of the canisters in winter, by the freezing of the water, a small quantity of alcohol is often added to the water before the canisters are soldered up. Messrs. Albright and Wilson avoid the use of much water in packing phosphorus by cutting a large cylindrical block of phosphorus into discs, each disc being then cut in a radial direction from the centre, and the pieces fitted into cylindrical tin canisters and covered with water.

Amorphous phosphorus may be prepared on a small scale by heating ordinary phosphorus for some time to a temperature of 260°, in a glass flask, the air of which has been expelled by carbonic acid. The glass flask is heated in an oil bath.

On the large scale this operation is conducted in an apparatus, patented by Albright of Birmingham, which consists of a cylindrical vessel of glass or porcelain, surrounded by a casing of cast iron fitting into a cast-iron sand bath, that stands in a cast-iron boiler containing an alloy composed of equal parts of lead and tin. A large hemispherical cast-iron dome covers the whole. The inner porcelain or glass vessel is also furnished with a lid connected with a spring in such a way that, in case of sudden internal pressure, the lid is raised, and the gas causing the pressure escapes. A tube furnished with a cock passes from the inner lid through the large outer arched dome, terminating in a vessel containing water or mercury, so that gases escaping from the glass or porcelain vessel may escape into the air without causing a return of air into the vessel. The apparatus is charged and set in action in the following way. Well-dried phosphorus is placed in the interior porcelain vessel, and the vessel containing the alloy of tin and lead heated by a fire underneath it. The alloy gradually melts, heating in succession the sand bath and the porcelain or glass vessel containing

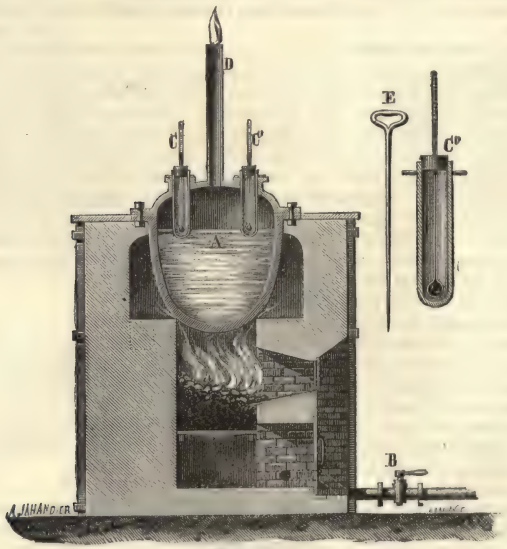


Fig. 99.

the phosphorus, driving out at first air, and afterwards gases which ignite spontaneously upon coming in contact with the air. The temperature of the metal bath is then brought up to 260°, and kept at this temperature until the conversion of the phosphorus into the amorphous condition is complete, a process which requires about 10 days. During the entire course of the operation the tube through which the gases escape from the interior vessel containing the phosphorus is kept hot by means of a lamp, so as to avoid stoppage from the condensation of any phosphorus that may distil over. When the operation is completed the cock of the delivery tube is closed so as to avoid the ingress of water from the receivers, or of air into the phosphorus vessel, upon the cooling down of the apparatus.

Coignet of Lyons prepares amorphous phosphorus by heating ordinary phosphorus in a cast-iron boiler, without employing either of the baths above described. The apparatus is shown in fig. 99. A is a crucible-shaped boiler of cast iron, standing in a furnace directly above the fire, the furnace being heated with coke. The tube (B)

serves for regulating the draught of air to the fire, and keeping the temperature of the boiler under control. The boiler is about two thirds filled with phosphorus, and gradually heated, the temperature being shown by four thermometers (c c'), which pass through the lid of the boiler. D is an iron tube for the exit of air and other gases. The evolution of gas at D must be moderate throughout the entire operation. Condensed products of distillation are pushed back into the boiler with the iron bar (E).

Purification.—Raw amorphous phosphorus always contains small quantities of ordinary phosphorus, which have to be removed by some process of purification. The raw amorphous phosphorus is cut into pieces and powdered under water. This powder is next dried and washed with carbon bisulphide, in which ordinary phosphorus is soluble. Since this method is somewhat dangerous, owing to the tendency to spontaneous combustion of carbon bisulphide containing phosphorus, raw amorphous phosphorus is purified in some places by roasting it in iron pans, the mass being constantly stirred. Ordinary phosphorus is thus burnt to phosphoric acid, which is afterwards washed out with water.

Coignet's method consists in boiling raw amorphous phosphorus with a solution of caustic soda, by which ordinary phosphorus is converted into sodium hypophosphite, which dissolves, and gaseous phosphoretted hydrogen, which escapes. The raw amorphous phosphorus is boiled with fresh quantities of caustic soda solution, until the unpleasant odour of phosphoretted hydrogen is no longer observed. It is then well washed with water and dried.

Nickles proposes shaking raw amorphous phosphorus with a solution of calcium chloride, having a specific gravity of from 1·83 to 1·85, which lies between that of ordinary phosphorus (1·83) and that of amorphous phosphorus (2·106). Ordinary phosphorus, therefore, collects on the surface of the solution, while the amorphous phosphorus sinks to the bottom, and is afterwards washed and dried; the ordinary phosphorus is removed with carbon bisulphide.

Uses.—The chief application of phosphorus is in the preparation of friction matches. The remaining consumption of phosphorus is for preparing various laboratory reagents, pharmaceutical preparations, poison for vermin, etc.

Friction Matches.—In prehistoric times fire was produced, as indeed it is at the present day among savages, by rubbing together two polished wooden surfaces. The production of fire by striking together flint and steel dates from the fourteenth century.

In 1805 an apparatus of peculiar construction was invented by Chancel, which consisted of a small bottle filled with asbestos that had been saturated with concentrated sulphuric acid. Splints partly coated with sulphur, and having the points coated with a mixture of sulphur and sugar, caught fire when pressed against the moist asbestos, the ignition being communicated to the splint by the sulphur covering.

In the year 1823 Döbereiner, at Jena, discovered that finely divided or spongy platinum possesses the property of igniting a mixture of atmospheric air and hydrogen. Döbereiner's apparatus has been already described on page 28. The apparatus is in use at the present day.

The first friction matches appeared in England in April 1827, and were the invention of a chemist and druggist named Walker, residing at Stockton. They consisted of thin slips of wood 2½ inches in length, covered with sulphur to one third their length, tipped probably with a mixture of sulphide of antimony, chlorate of potash and gum, and were sold for half-a-crown a box containing fifty matches. The London *Atlas* newspaper of January 10, 1830, describes them as being supplied in tin boxes, accompanied by a piece of glass paper, between the folds of which the match to be inflamed was pinched, and then suddenly drawn out. Phosphorus friction matches were not known on the continent until the year 1833, and, very curiously, several nations seem to have simultaneously produced this kind of match, so that it is difficult to say who was the discoverer of the first phosphorus matches. As early as 1815 Derosne appears to have been acquainted with the preparation of phosphorus matches. The first phosphorus matches consisted essentially of a mixture of phosphorus and potassium chlorate, and they were so dangerous that their manufacture was, in many countries, prohibited by law. The next attempt was made with a mixture of potassium chlorate, red lead, manganese, and phosphorus, which was succeeded by one consisting of lead peroxide and phosphorus, and finally of a mixture consisting of red lead, salpetre, and phosphorus. The modifications of modern date will be treated of further on.

The use of amorphous phosphorus instead of ordinary phosphorus is of great importance for this branch of industry, and although the consumption of this substance has not yet attained the dimensions which might be expected, still its advantages

over ordinary phosphorus are so great, that its consumption is sure before long to assume very considerable dimensions, and, probably, to exceed that of ordinary phosphorus. The use of amorphous phosphorus would prevent the terrible disease of the jaws from which the workpeople employed in the manufacture of matches containing ordinary phosphorus suffer, and besides this, cases of poisoning with the heads of lucifer matches would be rendered impossible.

The wood employed in the manufacture of matches is generally that of fir, pine, or aspen trees, less often poplar, birch, or beech, etc. The method of preparing the splints varies with the form to be given to them.

For the preparation of cylindrical splints a kind of plane is used, the edge of which is fluted, and it has a number of holes, generally three. When this plane is forced along a lath of wood, in a direction parallel to the fibres, the tool penetrates into the wood, cutting it up into cylindrical splints, each splint having a length equal to that of the lath taken. The lath is then again planed true with an ordinary plane, and the former operation repeated. This kind of work is generally conducted in the forest where the trees grow; thus, for instance, in the Black Forest, in several parts of Bohemia, and in Austria, etc.

The next operation, viz. that of cutting the splints into lengths suitable for the match manufacturer, is generally performed in the match factories. A machine of the kind consists of a narrow trough provided with a slit, in which works a knife moved by a lever. Wrana has invented an apparatus, by means of which manual skill is in part supplanted by machinery. The plane of this machine is impelled forwards by mechanism, and is simply guided by the workman. In Krutzsch's apparatus, manual labour is entirely supplanted by machinery. His machine consists of a steel plate, with about 400 holes placed as near together as possible; the edges of these holes are sharpened, and a block of wood is forced in the direction of the fibres against the plate, and thus divided into splints.

Sulphuration of the Splints.—For the purpose of sulphuring, the splints are packed in frames in such a way that when dipped in sulphur, sufficient room is left between each splint for the excess of sulphur to drop off. The frames are square, and consist of a number of parallel divisions, between which the splints are so laid that on one side of the frame their ends lie like the fibres of a brush. A single frame generally has 32 divisions, and each division holds 40 splints, making a total of 1,280 splints. The placing of the splints in the frame was formerly performed by hand, but at the present day a very ingeniously constructed apparatus is employed, which saves a considerable loss of time. The splints are made to fall, by a process of shaking, through the holes of a perforated metal plate, into the divisions in the frames, which are for this purpose slightly loosened. As soon as the frames are full, they are drawn together so as to secure the splints firmly, and removed.

The frames holding the splints are next placed in a horizontal position over melted sulphur, and lowered so that the protruding ends of the splints are covered to about $\frac{1}{8}$ in. with sulphur. The sulphur is contained in a shallow pan, the bottom of which consists of a perfectly even and horizontally placed stone slab, heated sufficiently to retain the layer of sulphur one-third of an inch deep, at a temperature of from 125°–130° C. The frames are so lowered into this sulphur trough that the ends of the splints just rest upon the bottom of the plate. The frames are then taken out, and the excess of sulphur adhering to the splints removed by shaking them, so that only a thin covering of sulphur adheres to each splint.

Matches are now often dipped in stearin or paraffin instead of sulphur, both of which are preferable to sulphur, as in burning they do not evolve the penetrating and disagreable smell afforded by it.

The tipping of the splints with the ignitable mixture is effected in the same way as that just described in coating with sulphur, etc., the only difference being that the layer of ignitable mixture is only $\frac{1}{8}$ in. in depth.

A special machine for dipping the splints in the ignitable composition has been constructed by Higgins. This consists of an endless chain, supporting the frames, which are thus drawn over the vessel containing the composition. In the ignitable composition itself is a rotating grooved roller, the grooves of which are filled with the mixture as it revolves, and the splints are caught one after the other, and are pressed by a special contrivance against the ignitable composition in the grooves of the roller. The entire apparatus is covered with a glass case, so as to shield the workmen from the injurious effects of phosphorus vapours.

The composition of the combustible composition varies considerably, being in part a trade secret, each manufactory having its own. The following tables will, however, serve to give some idea of the compositions most in use. Such compositions generally contain a small quantity of phosphorus, the chief mass consisting of oxidising substances, together with some adhesive substance, such as glue or gum. In this

country glue is generally used, in consequence of the liability of gum to absorb moisture from the air. Among the older recipes, by Böttcher, and which are now in part in use, are the two following:

I.		II.	
Phosphorus	4	Phosphorus	9
Saltpetre	10	Saltpetre	14
Red lead	3	Manganese peroxide	14
Glue	6	Gum	16

Payen obtained, by analysis, the following results:

	III.	IV.	V. Stearin dips
Phosphorus	2·5	2·5	3·0
Glue	2·0	Gum 2·5	2·5
Water	4·5	3·0	3·0
Fine sand	2·0	2·0	2·0
Red ochre	0·5	0·5	3
Cinnabar or Prussian blue	0·1	0·1	0·1–0·5
Potassium chlorate	—	—	3

German manufacturers, on the whole, use less phosphorus, as may be seen from the following analytical results:

VI:	
Phosphorus	4·7
Gum	14·0
Water	12·0
Red lead	40·0 } 'Oxidised
Nitric acid	25·0 } red lead.'

VII.		VIII.	
Phosphorus	8·0	Phosphorus	2·0
Glue	21·0	Glue	5·0
Lead peroxide	24·0	Chalk	3·0
Saltpetre	24·0	Lamp-black	0·12
		Manganese peroxide	1·0

When glue is used, it is cut in pieces and soaked in water for three hours, until it swells up. It is then brought into a boiler (A, fig. 100), heated by a water bath

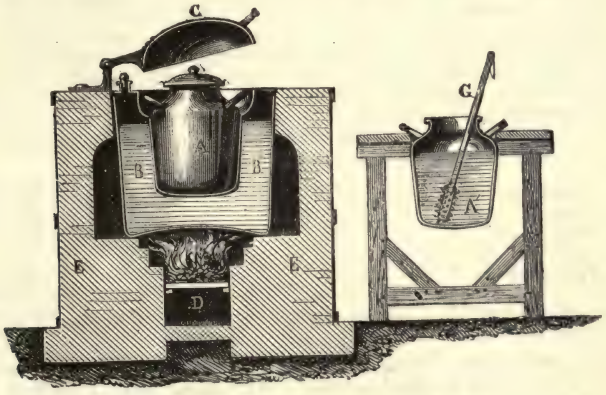


FIG. 100.

FIG. 101.

(B B) to 100°. When the glue has melted, the pot is taken out and placed upon a wooden frame (fig. 101), the phosphorus mixture is thrown into the pot, and the whole stirred with the stirrer (G) until cool. The stirrer is furnished with bristles, and by this means an emulsion of glue and phosphorus is produced, which is mixed with the sand, red lead, and other ingredients of the composition. The mass is then again heated in the water bath until liquid, when it is poured out upon the marble or stone plate used in the dipping process, and heated by a water bath placed beneath

it. When gum is used in the place of glue, the process is conducted in a similar way, the only difference being that it is not necessary to pour the mixture in a warm state upon the dipping plate, or to heat the latter.

Less phosphorus is required, according to Wagner, when the phosphorus has been previously dissolved in carbon bisulphide, and the other ingredients added to the solution. After the evaporation of the carbon bisulphide, the phosphorus remains in so fine a state of division, that it is very easily ignited. The recipe VII., above given, refers to a case of the kind. In some cases dextrin may conveniently take the place of glue or gum as adhesive material.

Drying of the Splints.—After the dipping is over, the splints are allowed to dry in the air for a short time. When glue has been used, the frames are hung out in the air for two or three hours; in cases where gum has been used the frames are exposed to the air for 24 hours. The preliminary drying is then succeeded by a more complete drying process, for which purpose the frames are hung upon iron supports in specially constructed drying rooms, constructed of fire-proof material, and heated by hot-water pipes laid along the floor. The floor is strewed with sand to a depth of 4 or 5 inches, so as to avoid the ignition of any matches that may have fallen on to the floor, should one get trodden on. The sand serves further to extinguish any fire that may break out. Each frame and its support is separated from its neighbour by a screen of sheet iron, so as to localise the fire in case of ignition.

When the combustible mixture has thoroughly dried, the splints are removed from the frames, and packed for exportation in paper, papier-mâché boxes, or in boxes of thin wood.

In order to prevent the matches from smouldering after the flame has been extinguished, Howse recommends soaking the splints, before dipping, in concentrated saline solutions for about 48 hours, and then drying them rapidly. The salts proposed are alum, sodium silicate, ammonium borate, ammonium sulphate, or ammonium phosphate, sal ammoniac, and zinc sulphate.

The precautions necessary in match manufactories cannot be overrated. Tubs filled with water ought to be placed in the rooms where phosphorus is handled, so that in case of an accident happening to a workman by the spirting of phosphorus, he may at once plunge the wound into cold water. Good ventilation also ought especially to be provided, for that alone can protect the workmen from disease and ill-health.

Matches without Sulphur.—It has been already mentioned above that the unpleasantness of sulphur matches may be avoided by dipping the splints in substances like stearin, paraffin, etc. instead of sulphur. The preparation of stearin matches will serve as an example of the process. The splints are fastened in the frames and their ends scorched by pressing them against hot iron plates. They are then dipped in shallow vessels lined with lead or tin, containing a layer of melted stearin $\frac{1}{8}$ to $\frac{1}{6}$ in. deep, which is kept hot meanwhile. The stearin is absorbed by capillarity into the pores of the wood, penetrating the entire lower extremity of the splints. The splints are allowed to remain a short time in the melted stearin, and are then tipped with combustible material in the usual way.

The ignition of the matches is faciliated by using a combustible composition containing less glue or gum, and more of oxidising substances; thus:

Phosphorus	3·0
Gum	0·5
Water	3·0
Sand	2·0
Lead peroxide	2·0

Instead of lead peroxide, a somewhat larger quantity of red lead and 0·5 parts of nitric acid may be substituted.

Wax or Vesta Matches.—These are prepared in the following way. A number of cotton wicks, from 100–200, wound round a large roller, are drawn through a bath of melted wax, or a mixture of 2 parts stearin with 1 part wax, the individual wicks being kept apart by a comb. Each wick is thus covered with a coating of wax, and they are next passed through a perforated iron plate, the opening of which corresponds with the thickness desired to be given to the taper. The tapers are then cut by machinery to the required length, packed in frames, and tipped in the usual way. These matches require a very readily ignitable tipping, since they are too weak to bear great pressure when rubbed.

The following composition of a mixture suitable for tipping wax matches is given by Merckel:

Phosphorus	12	
Gum	14	
Antimonous sulphide	3	
Red lead	35	'Oxidised red lead.'
Nitric acid	21	
Cinnabar	0·1	

Zulzer has constructed a machine by means of which the tapers are cut, fastened in frames, and then dipped, in one consecutive operation. The tapers are carried by machinery to holes in a moveable vertical iron table, which is connected with a cutting apparatus for dividing them into suitable lengths. The wicks when cut remain fast in these holes, and are carried away, by a mechanical contrivance, to be dipped, while a fresh perforated iron table takes the place of the one already filled.

Fusees for lighting cigars, etc., are prepared from paper or other combustible material which has been saturated with a solution of saltpetre, and thus rendered capable of burning in the open air.

Amorphous Phosphorus Matches.—In preparing these the splints are treated first of all with sulphur or stearin in the usual way, after which they are dipped into a combustible composition spread out upon a horizontal marble plate, to the depth of $\frac{1}{12}$ to $\frac{1}{8}$ in. To prepare the combustible composition, 40 parts of finely powdered potassium chlorate are thrown into 60 parts of a thick solution of gum, to which is then added 40 parts of amorphous phosphorus and 20 parts of powdered glass. When glue is used in the place of gum, it is softened by soaking in water for four or six hours, and then dissolved by heating it for fifteen or twenty minutes in a water bath to 50° or 60°. To 75 parts of glue solution are then added 40 parts of potassium chlorate, 40 parts of amorphous phosphorus, and 15 to 20 parts of powdered glass, the composition being spread out upon a marble plate, heated by steam to a temperature of 35° or 40°, and the splints dipped in the mixture. The drying process is effected in the usual way.

In 1853 Lundstrom, in Sweden, took out a patent for non-poisonous matches, which could only be ignited by rubbing them against a specially prepared surface. The splints are either covered first of all with sulphur, or are impregnated with stearic acid, wax, paraffin, etc., and are then dipped in the following composition:

Potassium chlorate	6
Antimonous sulphide	2–3
Glue	1

The surface against which the matches are rubbed is generally the side of the box, or a piece of paper, painted over with the following composition:

Amorphous phosphorus	10
Manganese peroxide or antimonous sulphide	8
Glue	3–6

Matches made in Paris, and known in the trade as androgynes, have their sulphured end covered with a mixture consisting of 2 parts potassium chlorate, 1 part charcoal, and 1 part umber, the composition being secured by glue, while their other end consists of amorphous phosphorus, also attached by means of glue. When required for use, a splint of the kind is broken in two, and the two opposite ends rubbed against one another.

Compounds.—Phosphorus forms a number of compounds with other elementary substances, but only a few of them possess any industrial importance. These compounds are generally termed phosphides, and they present considerable analogies to the corresponding compounds of nitrogen, arsenic, and antimony. This is especially evident in the gaseous compound of phosphorus and hydrogen PH_3, known as phosphine or phosphuretted hydrogen, which is closely analogous to ammonia, both in constitution and many other respects.

There is another compound of phosphorus and hydrogen represented by the formula PH_2. Phosphorus combines with chlorine in two proportions, forming a trichloride PCl_3, in which it is trivalent, and a pentachloride PCl_5, in which it is pentavalent. The bromine compounds are similarly constituted, and there is a triodide PI_3, as well as a diiodide PI_2, corresponding to the dihydride, but no pentiodide is known. The compounds with fluorine and cyanogen correspond to the trichloride. Phosphorus combines in several proportions with sulphur; it also combines with several of the metals, but these substances are very little known; they appear to be in some respects analogous to the sulphides in their general characters. The presence of a very minute proportion of phosphorus in some metals renders them hard and brittle (see 'Iron and Copper').

Besides the above-mentioned compounds of phosphorus with elementary substances

a number of substances are known by the general name of phosphorus bases, which are compounds of phosphorus with compound radicles or pseudo-elementary substances such as ethyl C_2H_5. These substances are analogous in constitution to ammonia or ammonium, and to the ammonia bases and other substances in which hydrocarbon compounds act the part of pseudo-elementary substances (see *ante*, pp. 39 and 69).

The most important compounds of phosphorus are the oxides. Two of these are known in the anhydrous state—the trioxide or phosphorous oxide P_2O_3, and the pentoxide P_2O_5, or phosphoric oxide; they both combine with water, forming hydrates or the hydrogen salts known as phosphorous acid H_3PO_3 and phosphoric acid H_3PO_4, and with basic oxides, constituting the corresponding saline substances known as phosphites and phosphates. A third oxide, P_2O, is known only in the state of combination either with basic oxides as hypophosphites, or with water, the hydrate or hydrogen salt being hypophosphorous acid.

	Hydrates		
	$P_2O\ 3H_2O$	=	$2\,H_3PO_2$ Hypophosphorous acid
Trioxide or phosphorous oxide P_2O_3	$P_2O_3 3H_2O$	=	$2\,H_3PO_3$ Phosphorous acid
Pentoxide or phosphoric oxide P_2O_5	$P_2O_5 3H_2O$	=	$2\,H_3PO_4$ Phosphoric acid

These three acids, which may be regarded as forming a series of oxides of phosphine PH_3, differ in respect to the hydrogen replaceable by metals. In hypophosphorous acid only one third of the hydrogen can be thus replaced, and the general formula of the hypophosphites is MH_2PO_2. In phosphorous acid two thirds of the hydrogen can be replaced by metals, and the general formula of the phosphites is M_2HPO_3; but in the acid corresponding to phosphoric oxide the whole of the hydrogen can be replaced by metals, and according to the amount actually replaced in this way three series of salts are formed, the composition of which, as compared with phosphoric acid, may be represented by the following formulæ:

Phosphoric acid	H_3PO_4
Neutral sodium phosphate	Na_3PO_4
Acid sodium phosphates	Na_2HPO_4, NaH_2PO_4

Besides the ordinary phosphoric acid there are at least two other hydrates of phosphoric oxide which differ from it in many respects, and constitute essentially distinct acids representing distinct series of salts.

Trihydrate	$P_2O_5 3H_2O$	=	$H_6P_2O_8$	or	$2\,H_3PO_4$	orthophosphoric acid
Dihydrate	$P_2O_5 2H_2O$	=	$H_4P_2O_7$			pyrophosphoric acid
Monhydrate	$P_2O_5\ H_2O$	=	$H_2P_2O_6$	or	$2\,HPO_3$	metaphosphoric acid

The metaphosphates containing one atomic proportion of a monovalent metal have the general formula MPO_3, those containing one atomic proportion of a divalent metal have the formula $M''P_2O_6$, and those containing one atomic proportion of a trivalent metal $M'''P_3O_9$. The metaphosphates are capable of combining with each other and forming a great number of double salts or polymeric compounds. There are four series of pyrophosphates which may be represented by the sodium salts:—

Neutral sodium pyrophosphate	$Na_4P_2O_7$
Acid sodium pyrophosphates	$Na_3HP_2O_7$, $Na_2H_2P_2O_7$, $NaH_3P_2O_7$

The neutral calcium salt is $Ca''_2P_2O_7$, and the neutral aluminum salt $Al''''_4P_6O_{21}$. The salts of the first three series may contain two or more different metals.

The characters of the three kinds of phosphoric acid and those of the corresponding salts are totally distinct; thus, for instance, metaphosphoric acid coagulates albumen, and the acid as well as its salts give a white precipitate with silver nitrate, while orthophosphoric acid does not coagulate albumen or give the same white precipitate with silver nitrate, and its salts give a bright yellow precipitate with silver nitrate. Pyrophosphoric acid does not coagulate albumen, and its salts give a white precipitate with silver nitrate. Both metaphosphoric acid and pyrophosphoric acid are readily converted into orthophosphoric acid by boiling their solutions in water. The corresponding salts are also converted into orthophosphates in the same way, or by fusion with excess of alkali.

CHLORINE.

Symbol Cl. Atomic Weight 35·5.

History.—This substance was discovered in 1774, by Scheele, who regarded it, according to the views then prevailing, as dephlogisticated hydrochloric acid. Berthollet held chlorine to be a compound substance, containing oxygen for one of its constituents and hydrochloric acid for the other. Gay-Lussac and Thénard were of the same opinion, or at least they did not consider chlorine to be an elementary substance. Sir H. Davy was the first to ascertain the real nature of chlorine, and it owes its name to him.

Occurrence.—Chlorine does not occur naturally in the free state; it exists, however, very abundantly in combination with other substances. Combined with hydrogen as hydrochloric acid, it occurs in the water of some volcanic springs; it occurs in very large quantities combined with sodium, as rock salt or common salt, either forming extensive beds, or in solution, as in sea-water and the water of springs. In combination with potassium, chlorine occurs as sylvin at Stassfurt and at Kalucz in Galicia; combined with magnesium it occurs in sea water, and in combination with potassium and magnesium, as carnallite, at Stassfurt and other places; in combination with ammonium or with calcium, chlorine also occurs in smaller quantities in volcanic exhalations, and in certain mineral waters.

Chlorine also occurs naturally in combination with the heavy metals, such as silver, lead, etc., but in comparatively small quantities. Chlorine is a never-failing constituent of the juices, etc., of both plants and animals; consequently it may be reckoned as one of the most widely diffused elements.

Characters.—Chlorine is at the ordinary temperature and pressure a greenish yellow gas. This character induced Sir H. Davy to give to it the name chlorine, from *χλωρός*, greenish-yellow. It has an unpleasant smell and exerts a powerful suffocating action, causing very dangerous irritation of the air passages, accompanied by violent coughing, and even expectoration of blood. The density of chlorine gas relatively to hydrogen is 35·5, and it has relatively to air a specific gravity of 2·442. At 0° and under a pressure of 6 atmospheres, it condenses, forming a liquid of dark greenish yellow colour, having in relation to water a specific gravity of 1·38. Chlorine has not yet been obtained in the solid condition. The solubility of chlorine gas in water varies with the temperature very considerably. At 0° water dissolves only 1·45 times its volume, and at 8° as much as 3·04 times its volume; at 17°, 2·37, at 35°C. 1·60, and at 50°C. 1·09 times its volume. Upon conducting chlorine gas into water cooled below 8°, there is formed a compound of chlorine with water, which has a composition represented by the formula $Cl\ 5H_2O$; it is a colourless crystalline substance, which decomposes at the ordinary temperature into chlorine and water. A solution of chlorine in water is decomposed by exposure to sunlight, yielding hydrochloric acid and oxygen gas, which escapes. On this account a solution of chlorine which, when freshly prepared, has a green colour, soon bleaches on exposure to light; hence it is necessary to keep solution of chlorine in a dark place.

The most important property of chlorine, or at least that to which it owes its use on a large scale, is the bleaching action it exerts upon vegetable colouring matters. This bleaching action of chlorine is due to its combination with hydrogen, which is a constituent of nearly all organic substances. Chlorine accordingly deprives all such organic substances of their hydrogen, producing indirectly oxidation, and thereby decomposing them. It is, however, capable of acting both as an oxidising and bleaching agent upon vegetable colouring matters by combining with the hydrogen of any water that may be present, thus liberating oxygen, which combines with the colouring matter.

Preparation.—Chlorine is prepared on a small scale by gently heating concentrated hydrochloric acid with pieces of manganese peroxide broken up to about the size

of a nut, in a good-sized glass flask. The reaction that takes place is represented by the equation—

$$\underset{146}{4HCl} + \underset{87}{MnO_2} = \underset{126}{MnCl_2} + \underset{36}{2H_2O} + \underset{71}{2Cl}$$

When chlorine ceases to be developed, the solution of manganese protochloride is poured off and fresh hydrochloric acid poured into the generating flask. In order to dry the gas, it is passed first through a Woulfe's bottle, contaning concentrated sulphuric acid, and then through one or two U tubes, filled either with pieces of calcium chloride or pumice stone saturated with concentrated sulphuric acid.

In the above method of preparing chlorine, half of the chlorine remains in combination with manganese. By acting upon common salt with sulphuric acid and manganese peroxide, the entire amount of chlorine contained in it may be liberated, according to the equation:

$$\underset{117}{2NaCl} + \underset{87}{MnO_2} + \underset{196}{2H_2SO_4} = \underset{151}{MnSO_4} + \underset{142}{Na_2SO_4} + \underset{36}{2H_2O} + \underset{71}{2Cl}$$

Practically three equivalents of sulphuric acid are taken, because sodium chloride is not entirely decomposed by sulphuric acid, except at very high temperatures, unless sulphuric acid be present in quantity sufficient to cause the formation of acid sodium sulphate. On a large scale, it is seldom customary to employ common salt and sulphuric acid, as the price of hydrochloric acid is now so very moderate. The use of magnesium chloride, which is now extremely cheap, would offer many advantages over the use of salt.

Several other methods of preparing chlorine have been proposed, of which the following are examples:—

Schlösing's method consists in acting upon manganese peroxide with a mixture of hydrochloric and nitric acids, the concentration being so regulated that chlorine only is evolved. The residue consisting of manganous nitrate, yielding upon calcination manganese peroxide and nitrous gas, which by contact with water yields nitric acid.

Mallet oxidises cuprous chloride by the oxygen of the air. This, when treated with hydrochloric acid, yields chlorine and cuprous chloride, which is again oxidised as before.

Schank's method consists in treating calcium chromate with hydrochloric acid, so as to produce chlorine, calcium chloride and chromium chloride, from which chromic oxide is precipitated by treatment with calcium carbonate, and the precipitate again converted into calcium chromate by igniting it with lime.

Dunlop's method consists in decomposing a mixture of common salt and sodium nitrate with sulphuric acid. Chlorine and nitrogen oxides are given off, and by passing the gas through sulphuric acid the nitrous compounds are absorbed and separated from the chlorine.

Deacon's method consists in decomposing hydrochloric acid by heating the gas in contact with atmospheric oxygen so as to form water with liberation of the chlorine. For this purpose a mixture of hydrochloric acid gas and air is passed through a chamber filled with lumps of porous clay heated to redness.

However, none of these methods have superseded the decomposition of hydrochloric acid by manganese peroxide.

For the preparation of chlorine on a large scale the apparatus consists either of a leaden still or, as shown from A to B in fig. 102, of several stoneware jars of 20 to 40

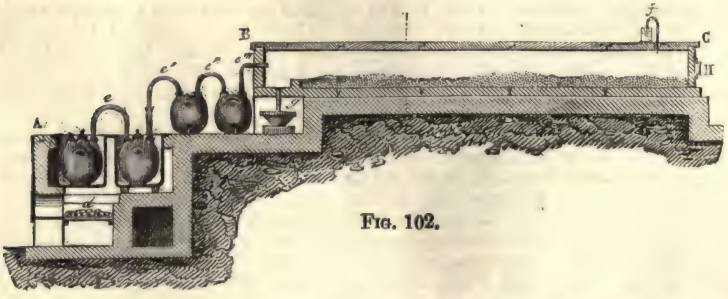


Fig. 102.

gallons capacity, fitted into cast-iron baths, which are either left empty or filled with water, and are heated by a fire (*d*). If a temperature a little above 100° C. is required, common salt, calcium chloride, or magnesium chloride is dissolved in the water of the

baths. The baths are sometimes heated by steam of high tension admitted through a rose into the water of the baths.

The generators are connected with each other by the tube (*e*) of lead or earthenware. For setting the process going, the generators are half filled with hydrochloric acid, the small openings closed, and after connecting them with the rest of the apparatus, perforated stoneware cylinders (M, fig. 103), containing pieces of manganese peroxide, are inserted into the neck of the generating vessels. These cylinders are closed below, and have two wide holes at the upper ends, which serve as a hold for the tongs (M, fig. 104), by means of which the cylinders are placed in, or removed from the generating vessels. As soon as the cylinders have been fitted into the generating vessels, the lids (N, fig. 103) are luted on, and the generators are heated at first gently, the heat being increased towards the end of the process. The gas evolved is conducted, so as to cool it, through the leaden tube (*e'*) into a stoneware vessel, and through the tube (*e''*) into another similar vessel, whence it passes to its final destination.

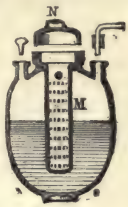


Fig. 103.



Fig. 104.

In manufactories where very large quantities of chlorine are employed, the generating stills consist of large cubical vessels of sandstone, holding 200 gallons and upwards. These chlorine stills are sometimes hewn out of a single stone block, or they are built of slabs and soaked with tar so as to enable them to resist the influence of the acid and the chlorine. They are heated either by passing steam into them, or into a jacket of the same material as that of which they are made. The generators are generally fitted with a grating, upon which the pieces of manganese peroxide are placed, or, as is sometimes the case, a number of perforated cylinders like that shown in fig. 103 are suspended in them, and they are closed by slabs of sandstone with manhole and delivery tubes. Since it is not possible to raise the temperature of these sandstone generators sufficiently high, the hydrochloric acid is not so completely decomposed in them as in the vessels of stoneware.

The residues from the chlorine generators may be used for purposes of disinfection, or the manganese may be precipitated with lime, and the precipitate calcined and used as a flux in blast furnaces in smelting iron.

The chief disadvantage attending the use of manganese peroxide arises from the difficulty of disposing of the residual liquor from the stills. This consists of a solution of manganous chloride, ferric chloride, and hydrochloric acid, and being of a noxious and destructive nature, it cannot be run into water-courses. Many attempts have therefore been made to convert the manganese it contains into peroxide that would be again available for producing chlorine.

Dunlop's Process.—Consists in treating the liquor with calcium carbonate in the cold, so as to precipitate the iron. After drawing off the liquor, the manganese is precipitated in the form of manganous carbonate by treatment with calcium carbonate under a steam pressure of two atmospheres. The precipitated manganous carbonate is washed, dried, and calcined in roasting furnaces, until carbonic acid is driven off, and it is converted by oxidation into peroxide, which is again available for use in the preparation of fresh quantities of chlorine.

Gatty's Process—Consists in evaporating the liquor to dryness with sodium nitrate and strongly heating the residue; by this means nitrous gases are evolved, which are used in the preparation of sulphuric acid, while manganese peroxide and sodium chloride remain behind. The sodium chloride is then either washed out from this mixture, or the mixture is used direct for preparing chlorine.

Hofmann's Process—Consists in precipitating the manganese with the liquor obtained by lixiviating soda waste; the precipitate, consisting of manganese sulphide, sulphur, and a small quantity of manganous oxide, is then decanted off, dried and roasted. The sulphurous oxide formed in this operation is conducted into vitriol chambers; the residue in the roasting ovens, consisting of manganous sulphate and manganous oxide and peroxide, is mixed with Chili saltpetre and heated to 300°; by this means sodium sulphate and manganese peroxide are formed, and the nitrogen peroxide given off is passed into vitriol chambers. The sodium sulphate is dissolved out and treated for soda, and the residue is used again for preparing chlorine.

Weldon's Method—Consists in precipitating the manganese as protoxide by means of lime and oxidising it by passing air through the mixture; a compound is thus formed containing about 70 per cent. of manganese peroxide. The precipitate is allowed to settle, and is used with hydrochloric acid for a further development of chlorine. The manganese peroxide as regenerated by Weldon's process has the advantage over

natural manganese that it is more easily and completely attacked by hydrochloric acid.

Weldon's method is now almost universally adopted in chemical works where chlorine is prepared. The first step is to separate the iron present as ferric chloride by adding to the hot liquor run off from the stills crushed limestone sufficient to neutralise free hydrochloric acid and convert the iron salt into ferric oxide, by a decomposition which takes place according to the following equation:

$$Fe_2Cl_6 + 3CaCO_3 = Fe_2O_3 + 3CaCl_2 + 3CO_2.$$

After the precipitated ferric oxide has subsided, the clear liquor containing manganous chloride $MnCl_2$, together with the calcium chloride formed by the neutralisation of the hydrochloric acid and the decomposition of ferric chloride, is run while still hot into tall cylindrical vessels fitted with pipes, through which a current of air can be forced into the liquor from a blowing engine. If the temperature of the liquor has fallen below 60°, steam is blown in to raise it to that degree; air is then forced in, and caustic lime mixed with water in a fine state of suspension rapidly added in quantity equal to 1·63 times the weight of the manganese in the liquor, by which means the manganous chloride is converted into a white precipitate of manganous oxide, according to the following equation:

$$\underset{126}{MnCl_2} + \underset{56}{CaO} = \underset{71}{MnO} + \underset{111}{CaCl_2}$$

Rather more than one third of the lime added remains mixed with the precipitated manganous oxide or dissolved in the hot solution of calcium chloride and communicating to the liquor a strong alkaline reaction. The precipitate gradually becomes darker, and after air has been blown into the mixture for some time it acquires a black colour, owing to the conversion of the manganous oxide into peroxide by the absorption of oxygen from the air injected. Meanwhile the alkaline reaction of the liquor diminishes, and at length entirely disappears when the absorption of oxygen ceases. A little more of the liquor containing manganous chloride is then run in, and after continuing the injection of air a few minutes longer, the contents of the vessel are run into a settling tank, where the manganese peroxide is deposited as a black mud, from which the clear solution of calcium chloride is drawn off.

The manganese peroxide thus obtained being in a very fine state of division, is acted upon by hydrochloric acid much more readily than the native peroxide, which is sometimes extremely compact and hard, and therefore, instead of adding hydrochloric acid to a charge of the recovered manganese peroxide, the stills are charged with hydrochloric acid and the moist precipitate is gradually run into the acid through openings in the covers of the stills.

The result obtained by this method differs in a very important particular from that produced by the oxidation of manganous oxide by exposure to atmospheric air. In the latter case the final product is not peroxide MnO_2, but manganic oxide Mn_2O_3, and moreover the conversion takes place very much more slowly than in the operation just described, the ultimate result being just the same as if only one half of the manganous oxide operated upon were converted into MnO_2, inasmuch as $Mn_2O_3 = MnO_2 + MnO$. Mr. Weldon considers that this is due to the fact that MnO_2 acts the part of an acid oxide like carbonic dioxide and combines with basic oxides, forming salts analogous to the carbonates. Hence in the oxidation of manganous oxide, in the absence of other basic oxides, the peroxide formed combines with an equivalent of manganous oxide, forming Mn_2O_3 and then the action stops. But when another basic oxide is present, such as lime or potash, the manganese peroxide formed combines with this oxide, forming $CaMnO_3$, and the whole of the manganous oxide is converted into peroxide. The presence of a basic oxide for the purpose appears therefore to be an essential condition of success in this operation, and it is for this reason that the excess of lime is added in precipitating the manganous oxide. The more intimate the mixture of the manganous oxide with the basic oxide that serves this purpose, the more readily does the absorption of oxygen take place. For this reason the effect is produced more rapidly in the presence of soda or potash, on account of their solubility; but fortunately the solubility of lime, in the hot solution of calcium chloride with which the manganous oxide is mixed in the precipitated liquor, is sufficient to ensure the practicability of this method of preparing manganese peroxide. The rapidity of the process may be judged of from Mr. Weldon's statement, that as much as two hundredweight of oxygen per hour may be thus absorbed from atmospheric air, and solidified in the condition of manganese peroxide.

In the product actually obtained on the large scale, water appears to some extent to act the part of the base with which the manganese peroxide is combined, and the action that takes place may be represented by the following equation:

$2MnO + H_2O + CaO + 2O = CaH_2MnO_3$ or $CaMnO_3 + H_2MnO_3$

and this product, in the dry state, would contain 70 per cent. manganese peroxide.

Uses.—Chlorine is principally used for bleaching substances made from vegetable fibres, such as cotton and linen, also in paper manufactories for removing the colouring matters from dyed or stained stuffs; also in preparing potassium chlorate and the double aluminum and sodium chloride, and in the manufacture of aluminum, in preparing iodine, chloroform, red prussiate, for the extraction of gold, and for disinfecting purposes. It is also much used as a reagent in chemical laboratories. Greater part of the chlorine produced in chemical works is converted into a portable state by bringing the gas in contact with hydrate of lime, which absorbs it in large amount, forming what is termed bleaching powder.

In the same way that chlorine destroys organic colouring matters, so does it act upon bad-smelling gases and miasmas, whence its use as a disinfectant.

Chlorine gas is very suitable for disinfecting large chambers, and for this purpose it may be prepared on the spot by warming a mixture of manganese with concentrated hydrochloric acid in an earthen pan.

Compounds.—Chlorine combines with most other elementary substances, forming substances which are termed chlorides. The chlorides of monatomic metals contain equal atomic proportions of chlorine and metal, and correspond to hydrogen chloride or hydrochloric acid. The chlorides of polyatomic elements contain two, three, four, five, or more atomic proportions of chlorine, according to the atomicity of the particular elementary substances with which it is combined. These are distinguished in the same way as oxides by adding to the name of the elementary substance they contain in common the terminations ous and ic, as ferrous chloride and ferric chloride. The formulæ in the following table represent the composition of the more important chlorides of the elementary substances:

Hydrogen		HCl							
Sodium		NaCl							
Potassium		KCl							
Silver	Ag_4Cl_2	AgCl							
Calcium			$CaCl_2$						
Strontium			$SrCl_2$						
Barium			$BaCl_2$						
Magnesium			$MgCl_2$						
Zinc			$ZnCl_2$						
Copper	Cu_2Cl_2		$CuCl_2$						
Mercury	Hg_2Cl_2		$HgCl_2$						
Lead			$PbCl_2$						
Manganese			$MnCl_2$					Mn_2Cl_6	MnCl.
Iron			$FeCl_2$					Fe_2Cl_6	
Nickel			$NiCl_2$						
Cobalt			$CoCl_2$					Co_2Cl_6	
Chromium			$CrCl_2$					Cr_2Cl_6	
Uranium			UCl_2						
Aluminum								Al_2Cl_6	
Palladium			$PdCl_2$		$PdCl_4$				
Platinum			$PtCl_2$		$PtCl_4$				
Tin			$SnCl_2$		$SnCl_4$				
Bismuth			$BiCl_2$	$BiCl_3$					
Antimony				$SbCl_3$		$SbCl_5$			
Arsenic				$AsCl_3$					
Phosphorus				PCl_3		PCl_5			
Nitrogen				NCl_3					
Boron				BCl_3					
Iodine				ICl_3	ICl_4				
Gold		AuCl		$AuCl_3$					
Tungsten			WCl_2		WCl_4	WCl_5			WCl_6
Molybdenum			$MoCl_2$		$MoCl_4$				
Tellurium									
Sulphur	S_2Cl_2				SCl_4 (?)				
Titanium					$TiCl_4$			Ti_2Cl_6	
Silicon					$SiCl_4$				
Carbon	C_2Cl_2			C_2Cl_4	CCl_4			C_2Cl_6	

Three oxides of chlorine are known; the monoxide Cl_2O or hypochlorous oxide,

the trioxide Cl_2O_3 or chlorous oxide, and the tetroxide Cl_2O_4, the first two forming saline compounds with water and basic oxides, known as hypochlorites and chlorites, the respective hydrogen salts being hypochlorous acid HClO and chlorous acid $HClO_2$. Two other oxides are known only in combination with hydrogen and metals as chlorates and perchlorates, the hydrogen salts being chloric acid $HClO_3$ and perchloric acid $HClO_4$. The relations of these oxides to each other and to their hydrogen salts are shown in the following table:

Hypochlorous oxide	$Cl_2O + H_2O = 2HClO$	Hypochlorous acid
Chlorous oxide	$Cl_2O_3 + H_2O = 2HClO_2$	Chlorous acid
Chlorine tetroxide	Cl_2O_4	
Chloric oxide ?	$Cl_2O_5 + H_2O = 2HClO_3$	Chloric acid
Perchloric oxide ?	$Cl_2O_7 + H_2O = 2HClO_4$	Perchloric acid

The hypochlorites are soluble in water, and readily undergo decomposition, evolving oxygen; the solutions oxidise many substances, and have the power of bleaching; when solutions of hypochlorites are heated to boiling these salts are converted into chlorate and chloride, according to the following equation:

$$3KClO = KClO_3 + 2KCl.$$

These salts are the essential constituents of the bleaching preparations made by saturating alkaline solutions or lime hydrate with chlorine.

The alkaline hypochlorites are only known in solution; any attempt to evaporate these solutions causing decomposition. These solutions are colourless when pure, but more generally they have a yellow colour, due to the presence of free hypochlorous acid; they evolve an odour of this acid, and are used for purposes of bleaching and disinfecting. The solution of potassium hypochlorite is known under the name of eau de Javelle; that of sodium hypochlorite under the name of eau de Labarraque; and the calcium compound, either combined or mixed with calcium chloride, is known as chlorinated lime or bleaching powder (see 'Bleaching Preparations').

Hypochlorous acid is a yellowish volatile liquid, having an acrid taste and a sweetish odour. In a concentrated state it decomposes rapidly, and even the dilute acid is decomposed by heat into chloric acid, chlorine, oxygen and water; it is a powerful bleaching and oxidising agent.

Hypochlorous acid or an acidified solution of a hypochlorite reacts with chlorides and liberates chlorine from both, according to the equation:

$$KClO + 2HCl = KCl + H_2O + 2Cl.$$

The chlorites are soluble salts having bleaching properties, but they have no industrial significance.

The chlorates are also soluble salts of greater stability than chlorates or hypochlorites, but they have no bleaching power. At a high temperature chlorates are decomposed, generally with evolution of oxygen and formation of perchlorate, sometimes also with evolution of chlorine; they are therefore powerful oxidising agents, and when mixed with carbonaceous substances, sulphur, etc., give rise to violent explosion on the application of heat or even by rubbing the mixtures. Chloric acid is a colourless syrupy liquid, having a strong acid reaction, and when warm a pungent odour resembling that of chlorine. It is a powerful oxidising and bleaching agent, and decomposes when heated, with evolution of oxygen and chlorine and formation of perchloric acid.

The perchlorates are of little importance industrially; they are mostly soluble in water—the potassium salt only sparingly—and are more stable than any of the previously mentioned salts of chlorine oxides. The acid is a colourless volatile liquid that oxidises carbonaceous substances with violent explosion, but does not bleach; it is very corrosive and forms a crystallisable hydrate.

BLEACHING PREPARATIONS.

The power which chlorine possesses of destroying vegetable colours was observed by Berthollet very soon after the discovery of this substance by Scheele, and attempts were made to apply it in bleaching linen. It was soon found that chlorine could be most conveniently used for this purpose when dissolved in an alkaline solution; and in 1799 the use of dry hydrate of lime in place of solution of potash or milk of lime was introduced by Macintosh for preparing bleaching powder or chlorinated lime. The exact chemical nature of this material is somewhat uncertain, but it may be regarded as consisting essentially of a compound or a mixture of calcium hypochlorite with cal-

cium chloride. It is formed by the action of chlorine upon lime, which, for this purpose, must be employed either as solid hydrate or in the condition known as milk of lime. The chemical change which takes place is represented by the following equation:

$$2CaH_2O_2 + 4Cl = CaCl_2 + 2H_2O + CaCl_2O_2.$$

However, chlorinated lime has never a composition exactly like that shown in the above equation, corresponding to 49 per cent. of chlorine, but always contains water and an excess of hydrate of lime, which is necessary for preventing its too quick decomposition. The actual amount of chlorine seldom exceeds 35 per cent.

The solutions of alkaline hypochlorites are prepared by passing chlorine gas from generators of the form shown in fig. 103 into carboys containing a solution of sodium carbonate or potassium carbonate in from 6 to 10 parts of water. The introduction of chlorine is attended with evolution of carbonic acid gas, the reaction being represented by the equation:

$$K_2CO_3 + 2Cl = KClO + KCl + CO_2.$$

The operation should be stopped before all the carbonic acid has been driven off, and it is necessary that at the end of the reaction about 5 per cent. of alkaline carbonate should remain undecomposed, or rather in the state of acid carbonate.

The alkaline hypochlorites are sometimes prepared with bleaching powder, by mixing solutions of 20 parts of crystallised soda, or 12 parts of potash, in 100 parts of water, with a filtered solution of 10 parts of strong chlorinated lime. By the reaction of calcium hypochlorite with the alkaline carbonates, insoluble calcium carbonate is precipitated, and the alkaline hypochlorites remain in the solution which is then decanted from the insoluble calcium carbonate.

Characters.—Chlorinated lime or bleaching powder is a white and somewhat moist powder, which, when left to itself, undergoes gradual decomposition. Properly prepared, it ought not to lose more than 3 or 4 per cent. of chlorine in the course of a year. When chlorinated lime is treated with acids, chlorine is evolved, as shown by the following equations, and the decomposition takes place in two consecutive stages, hypochlorous acid being formed in the first instance:

$$CaCl_2O_2 + H_2SO_4 = CaSO_4 + 2HClO,$$

and when sufficient excess of hydrochloric acid is present both substances are resolved into water and chlorine, $HClO + HCl = H_2O + 2Cl$. The application of a strong heat to chlorinated lime causes decomposition of the calcium hypochlorite into oxygen and calcium chloride ($CaCl_2O_2 = CaCl_2 + 2O$); oxygen is also evolved from chlorinated lime when a solution in water is mixed with hydrated oxides, such as hydrated ferric iron or cupric oxide. Sunlight also exerts a decomposing influence upon bleaching powder, and in manufactories where it is produced it is at once packed into casks. Even then bleaching powder undergoes decomposition, and might give rise to dangerous explosions if packed in a close vessel.

In preparing solid chlorinated lime the purest lime is chosen, and especial care is taken that it does not contain iron, which would render the bleaching powder dirty in colour, or magnesia, which would render it too hygroscopic, owing to the formation of magnesium chloride.

Slaking of the Lime.—This operation is performed either by spreading out pieces of lime and sprinkling them with water until they have crumbled away into a fine powder, or the pieces are held in a sieve in water until they show signs of energetic combination taking place. The slaked mass is then spread out, sprinkled once or twice with some water, and made up into a layer 1½ in. in height, in which condition it is allowed to lie for some days and then sifted. The product obtained by this operation when properly prepared contains between 6 and 12 per cent. of moisture.

Absorption of the Chlorine.—The arrangement shown in fig. 102 from B to C is very often used for this purpose. It consists of a rectangular chamber, about 13 feet long, 3½ feet wide, 2 feet high. The sides are formed either of sandstone plates, or of iron plates covered with bitumen, sometimes of well-tarred wood or of slates, or thick brickwork arched over. At the entrance of the chamber is a kind of gutter running in a diagonal direction, serving to collect and run off condensed liquid products. At the opposite end is a door (H), and on the roof of the chamber a safety valve (*f*). Slaked lime in fine powder is strewn upon the floor of the chamber, which must be perfectly even, a layer being formed about 6 or 8 inches in thickness.

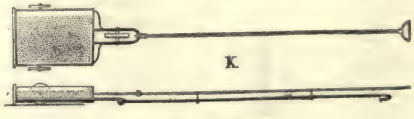


FIG. 105.

The charging is effected either through holes at the sides of the chamber, that can be hermetically closed, or by means of a small truck of sheet iron (fig. 105, K), holding enough to cover an area of $3\frac{1}{4}$ feet, and fitted with a sliding bottom. This truck is pushed in as far as the gutter at the end opposite to the door (H), and the bottom of the truck is then drawn away, leaving the charge of lime behind. The opening at H is then closed, the lid fitted on air-tight, and chlorine is passed into the chamber either through the five openings (*e'''*, fig. 106), or through a wide tube fitted into the cover of the chamber. Chambers in which the lime is spread upon tables or hurdles have of late fallen into disuse, since it has been found that the chlorine acts quite as well when the lime is simply spread upon the floor. The dimensions of these chambers are sometimes much larger.



FIG. 106.

Method of Conducting the Process.—Chlorine is passed into the chambers very slowly during the first 18 or 20 hours, as the reaction causes a considerable rise of temperature, and when the temperature rises above 90°, the calcium hypochlorite is decomposed into calcium chlorate and chloride. It is not usual to allow the temperature to rise above 25°. The completion of the process may be ascertained either by examining the gas escaping from the valve (*f*), which must bleach blue litmus paper, or from the amount of chlorine generated, which may be judged of by the quantity of materials used. The longer the chlorine is allowed to react the more slowly is it absorbed: but it is never passed in until no further absorption takes place, for in that case the bleaching powder would be far too rich in chlorine, and very liable to decomposition. The proper amount of chlorine in bleaching powder is from 33 to 35 per cent.

In an apparatus of the above kind it is possible, with a superficial area of about 44 square feet, to convert 300 lbs. of lime in 24 hours into 440 lbs. of chlorinated lime; so that a manufactory furnished with 20 separate sets of apparatus can produce every 24 hours about 4 tons of bleaching powder.

In preparing liquid chlorinated lime, chlorine is passed into milk of lime contained in sandstone tanks, closed above air-tight with boards so as to prevent the escape of gas. The gas is simply passed to the surface of the liquid, which is continually stirred by a special contrivance.

Gay-Lussac's method of determining the percentage of chlorine in chloride of lime depends first upon the oxidising action of chlorine in presence of water upon arsenous acid, and the formation of arsenic acid according to the equation:

$$\underset{198}{As_2O_3} + \underset{142}{4Cl} + 2H_2O = \underset{230}{As_2O_5} + 4HCl;$$

and, secondly, upon the fact that a mere trace of free chlorine suffices to decolorise tincture of indigo.

From the above equation it will be seen that one molecule of arsenous acid requires four atomic proportions of chlorine for its conversion into arsenic acid. When therefore a solution containing a known quantity of arsenous acid is mixed with a solution of bleaching powder, until all the arsenous acid is converted into arsenic acid, the amount of active chlorine contained in the bleaching powder may be calculated from the quantity of bleaching powder required. The point of complete oxidation of the arsenous acid is ascertained by adding to the solution of arsenous acid a small quantity of a solution of indigo, which is decolorised the moment all the arsenous acid is oxidised.

The arsenous acid solution is prepared for this purpose by dissolving 13·94 grms. of pure arsenous acid in a small quantity of caustic potash solution, acidulating the solution with hydrochloric acid, and diluting with water to one litre. 1 c.c. of this solution then contains 0·01394 grm. of arsenous acid, which corresponds to 0·01 grm. of chlorine.

The operation is conducted as follows: 10 grms. of the sample are triturated in a porcelain mortar with distilled water, the solution decanted off and the operation repeated with fresh quantities of water several times. The decanted portions of the liquid are then collected in a litre flask (A, fig. 107), furnished with an accurately fitting stopper, the flask filled up to the mark with water and its contents shaken up. The next step is to place 10 c.c. of the solution of arsenous acid (corresponding to 0·1394 grm. of As_2O_3, or 0·1 grm. Cl) in a glass vessel (B, fig. 108). The arsenous acid solution is kept in a bottle (C, fig. 110), fitted with a pipette (D), by means of which it can be measured out. The arsenous acid solution in



FIG. 107.



FIG. 108.

the vessel (B) is diluted with ten times its volume of distilled water, and a single drop of tincture of indigo added. The solution of bleaching powder prepared in the way above described is again shaken up and a portion drawn off into the burette (E, fig. 109), which holds from 50—100 c.c., and is divided into divisions of $\frac{1}{10}$ c.c. This solution of bleaching powder is then allowed to drop from the burette into the solution of arsenous acid until the indigo begins to decolorise, the operation being aided by continual stirring with a glass rod.



Fig. 109.



Fig. 110.

Supposing that 30 c.c. of such a solution of bleaching powder be required for the complete oxidation to arsenic acid of the ·1394 grm. of arsenous acid contained in 10 cubic centimetres of the arsenous acid solution; this quantity requires for its oxidation 0·1 grm. of chlorine; the 30 c.c. bleaching powder solution would represent 0·30 grm. of solid chlorinated lime, and accordingly the amount of active chlorine would be 33·33 per cent.:

$$0{\cdot}30 : 0{\cdot}1 = 100 \cdot x; \; x = 33{\cdot}33.$$

Penot and Mohr's method consists in treating a measured volume of the bleaching powder solution with a known quantity of an alkaline solution of sodium arsenite in excess; the arsenous acid remaining unaltered is determined by adding to the liquid a small quantity of starch-paste, and titrating with a solution of iodine of known strength until the blue coloration of the starch by iodine takes place. This cannot occur until the whole of the arsenous acid present has been converted into arsenic acid. In carrying out this test the following liquids are required:—

1. A solution of bleaching powder prepared in the way above described.

2. A solution of arsenous acid (sodium arsenite). In preparing this, 4·436 grms. of very pure arsenous acid is dissolved in water containing 25 grms. of crystallised sodium carbonate, and then diluted to the volume of 1 litre. 1 c.c. of this solution contains 0·004436 grm. of arsenous acid and represents 1 c.c. of chlorine gas. This solution of sodium arsenite requires to be kept in small, well-closed bottles, which ought to be quite full, so as to prevent the formation of sodium arsenate by oxidation.

3. Iodine Solution. This is prepared by dissolving 11·38 grms. of dry iodine in as small a quantity as possible of potassium iodide, the solution being made up to a litre with distilled water. Since iodine in the presence of water oxidises arsenous acid just like chlorine, 4 atomic proportions of iodine correspond to 1 molecule of arsenous acid, or, in other words, 4·436 grms. of arsenous acid corresponds to 11·38 grms. of iodine (198 : 508 = 4·436 : 11·38); or, 1 c.c. of the solution of sodium arsenite corresponds to 1 c.c. of the solution of iodine. On testing the solution of iodine, 10 c.c. of the solution of sodium arsenite are measured into a beaker by means of a pipette, mixed with some starch paste, then diluted with water, and solution of iodine added in quantity sufficient to cause blue coloration. 10 c.c. of solution of iodine ought to be required, and should this not be the case, the corresponding correction must be made in the final calculation of results.

4. Starch Paste. This ought to be very dilute, and freshly prepared.

The re-agents being prepared in the way above described, the process of testing is conducted in the following manner. 50 c.c. of the solution of bleaching powder are drawn off from a pipette into a beaker glass; an excess of sodium arsenite solution is added, as well as a small quantity of starch paste, and solution of iodine is then dropped into the mixture until a blue coloration sets in. The number of c.c. of iodine solution used is then deducted from the number of c.c. of sodium arsenite taken, the difference being the number of c.c. of sodium arsenite oxidised by the bleaching powder. Supposing the difference found to be 45 c.c., this would correspond to 45 c.c. of chlorine, since 1 c.c. of the solution of sodium arsenite corresponds to 1 c.c. of chlorine. The 50 c.c. of bleaching powder solution representing ·5 grm. of solid chloride of lime, therefore, contains 45 c.c. of active chlorine. Accordingly 1000 grms. or 1 kilo of bleaching powder contains 90,000 c.c. or 90 litres of chlorine gas; *i.e.* the bleaching powder shows a strength of 90°.

The chlorometrical degrees represent the number of litres of chlorine contained in 1 kilo of bleaching powder. By multiplying the chlorometrical degrees by 3·178 (the weight of 1 litre of chlorine gas in grammes) and dividing by 10, the per-centage by weight is obtained. On the contrary, the chlorometrical degrees are obtained by dividing the percentage by weight by 0·3178.

The manganese peroxide that is used in the production of chlorine is tested in a similar manner. The relative value of a sample of it depends upon the amount of

peroxide present, or, in other words, upon the extent to which the material is capable of liberating chlorine by reaction with hydrochloric acid. Hence the valuation of the manganese peroxide of commerce may be effected by determining according to either of the foregoing methods the amount of chlorine obtained with a given weight of the manganese. (See article 'Manganese.')

Uses.—Chlorinated lime is used for the same purposes as chlorine, since it readily evolves chlorine gas when treated with dilute acids, and from its portability it is better suited for some purposes than chlorine gas prepared directly. It is on this account extensively employed in the bleaching of textile fabrics and in calico printing, etc.

Chlorinated lime is also much employed for disinfecting rooms, which are either sprinkled with the powder, or the floors, walls, etc. are washed with a solution of this disinfectant. Pettenkofer is opposed to the disinfection of privies with chlorinated lime

HYDROCHLORIC ACID.

FORMULA HCl. MOLECULAR WEIGHT 36·5.

History.—Basil Valentine, who lived in the fifteenth century, first described the preparation of pure aqueous hydrochloric acid. Before his time a mixture of hydrochloric acid with nitric acid had been known under the name of aqua regia, its preparation having been described by the Arabian chemist Geber in the eighth century. In former times the general name for this substance was spirit of salt, a name which is not quite extinct at the present day. Later, it received the name of muriatic acid, and it is now generally called hydrochloric acid. After various hypotheses had been set up as to its composition, its true composition was discovered by Davy in 1810.

Occurrence.—Hydrochloric acid occurs naturally in the exhalations of volcanoes, and thence it finds its way into streams in their neighbourhood. Besides this it is always present in small quantities in the gastric juice of animals.

Composition.—Hydrochloric acid is a compound of hydrogen with 35·5 times its weight of chlorine. In the gaseous state it contains half its volume of hydrogen.

Characters.—In the anhydrous state hydrochloric acid is a colourless gas of very penetrating order, which forms a thick cloud when allowed to escape into the air. The density of the gas relatively to hydrogen is 18·25, and relatively to air it has a specific gravity of 1·255. Under a pressure of 30 to 40 atmospheres, or when cooled to −50°, at the normal pressure, it condenses to a colourless liquid. It is one of the most soluble of gases, water dissolving at 0°, and under the normal atmospheric pressure 500 times its volume of the gas, and at 15° 475 times its volume. When water saturated with hydrochloric acid gas is heated to the boiling point, a large part of the hydrochloric acid escapes; but part remains as a solution, containing 20 per cent. of acid, which has a specific gravity of 1·10; boils at 110°, and distils over. The ordinary liquid hydrochloric acid of commerce is a solution of the gas in water; and since the specific gravity of this solution increases in proportion to the amount of gas it contains, a determination of the specific gravity of samples of commercial acid affords an excellent means of ascertaining their strength.

The strength of hydrochloric acid is often expressed in degrees of Baumé's or Twaddle's hydrometer. The following table serves for ascertaining the strength of samples of acid from the degrees of either hydrometer:

Degrees Baumé	Degrees Twaddle	Percentage of Hydrochloric acid	Degrees Baumé	Degrees Twaddle	Percentage of Hydrochloric acid
26	42	42·85	14·5	20	20·20
25	40	40·80	12	18	18·18
24	38	38·88	11	16	16·16
23	36	36·36	10	14	14·14
22	34	34·34	9	12	12·12
21	32	32·32	8	10	10·10
20	30	30·30	6	8	8·08
19	28	28·28	5	6	6·06
18	26	26·26	3	4	4·04
17	24	24·24	2	2	2·02
15·5	22	22·22			

The following table gives the contents in chlorine and hydrochloric acid gas of aqueous solutions of hydrochloric acid.

Acid of 1·2 sp. gr.	Specific gravity	Chlorine	Hydrochloric acid gas	Acid of 1·2 sp. gr.	Specific gravity	Chlorine	Hydrochloric acid gas
100	1·2000	39·675	40·777	50	1·1000	19·837	20·388
99	1·1982	39·278	40·369	49	1·0980	19·440	19·980
98	1·1964	38·882	39·961	48	1·0960	19·044	19·572
97	1·1946	38·485	39·554	47	1·0939	18·647	19·165
96	1·1928	38·089	39·146	46	1·0919	18·250	18·787
95	1·1910	37·692	38·738	45	1·0899	17·854	18·359
94	1·1893	37·296	38·330	44	1·0879	17·457	17·941
93	1·1875	36·900	37·923	43	1·0859	17·060	17·534
92	1·1857	36·503	37·516	42	1·0838	16·664	17·126
91	1·1846	36·107	37·108	41	1·0818	16·267	16·718
90	1·1822	35·707	36·700	40	1·0798	15·870	16·310
89	1·1802	35·310	36·292	39	1·0778	15·474	15·902
88	1·1782	34·913	35·884	38	1·0758	15·077	15·494
87	1·1762	34·517	35·476	37	1·0738	14·680	15·087
86	1·1741	34·121	35·068	36	1·0718	14·284	14·679
85	1·1721	33·724	34·660	35	1·0697	13·887	14·271
84	1·1701	33·328	34·252	34	1·0677	13·490	13·863
83	1·1681	32·931	33·845	33	1·0657	13·094	13·456
82	1·1661	32·535	33·437	32	1·0637	12·697	13·049
81	1·1641	32·136	33·029	31	1·0617	12·300	12·641
80	1·1620	31·746	32·621	30	1·0597	11·903	12·233
79	1·1599	31·343	32·213	29	1·0577	11·506	11·825
78	1·1578	30·946	31·805	28	1·0557	11·109	11·418
77	1·1557	30·550	31·398	27	1·0537	10·712	11·010
76	1·1536	30·153	30·990	26	1·0517	10·316	10·602
75	1·1515	29·757	30·582	25	1·0497	9·919	10·194
74	1·1494	29·361	30·174	24	1·0477	9·522	9·786
73	1·1473	28·964	29·767	23	1·0457	9·125	9·379
72	1·1452	28·567	29·359	22	1·0437	8·729	8·971
71	1·1431	28·471	28·951	21	1·0417	8·332	8·563
70	1·1410	27·772	28·544	20	1·0397	7·935	8·155
69	1·1389	27·376	28·136	19	1·0377	7·538	7·747
68	1·1369	26·979	27·728	18	1·0357	7·141	7·340
67	1·1349	26·583	27·321	17	1·0337	6·745	7·932
66	1·1328	26·186	26·913	16	1·0318	6·348	6·524
65	1·1308	25·789	26·505	15	1·0298	5·957	6·116
64	1·1287	25·392	26·098	14	1·0279	5·554	6·709
63	1·1267	24·996	25·690	13	1·0259	5·158	5·301
62	1·1247	24·599	25·282	12	1·0239	4·762	5·893
61	1·1226	24·202	24·874	11	1·0220	4·365	4·486
60	1·1206	23·805	24·466	10	1·0200	3·968	4·078
59	1·1185	23·408	24·058	9	1·0180	3·571	3·670
58	1·1164	23·012	23·150	8	1·0160	3·174	3·262
57	1·1143	22·615	23·242	7	1·0140	2·778	3·854
56	1·1123	22·218	22·834	6	1·0120	2·381	3·447
55	1·1102	21·822	22·426	5	1·0100	1·984	2·039
54	1·1082	21·425	22·019	4	1·0080	1·588	2·631
53	1·1061	21·028	21·611	3	1·0060	1·191	1·224
52	1·1041	20·632	21·203	2	1·0040	0·795	1·316
51	1·1020	20·235	20·796	1	1·0020	0·397	1·408

Commercial hydrochloric acid is when pure a colourless liquid, which fumes in contact with moist air. When the degree of concentration is as low as 20 per cent. of gaseous acid this fuming ceases. Raw commercial hydrochloric acid is generally of a yellow colour, owing to the presence of ferric chloride. Besides this latter impurity, commercial hydrochloric acid often contains chlorine, sulphurous oxide, and sulphuric acid, as well as sodium chloride and sulphate. When arsenical sulphuric acid has been employed in the manufacture of hydrochloric acid, the arsenic passes into the hydrochloric acid, and since large quantities of sulphuric acid are now manu-

factured from pyrites, the presence of arsenic in common commercial hydrochloric acid is a matter of frequent occurrence. Selenium compounds are also often found in commercial hydrochloric acid.

Preparation.—Hydrochloric acid is generally prepared by heating together equivalent proportions of common salt and sulphuric acid, the ultimate result of the decomposition being represented by the following equation:

$$\underset{117}{2NaCl} + \underset{98}{H_2SO_4} = \underset{142}{Na_2SO_4} + \underset{73}{2HCl}$$

Therefore, in preparing hydrochloric acid, it would be necessary to take 117 parts by weight of sodium chloride to every 98 parts by weight of concentrated sulphuric acid; but as sulphuric acid generally contains rather more than 1 molecule of water, it is usual to take more of it than the quantity above indicated.

The reaction between these substances may be more correctly represented as taking place in two stages, there being formed in the first instance acid sodium sulphate and hydrochloric acid, according to the equation—

$$\underset{58{\cdot}5}{NaCl} + \underset{98}{H_2SO_4} = \underset{120}{NaHSO_4} + \underset{36{\cdot}5}{HCl}$$

and then the heat being increased towards the end of the process, the acid sodium sulphate decomposes a further quantity of salt, according to the equation—

$$\underset{58{\cdot}5}{NaCl} + \underset{120}{NaHSO_4} = \underset{142}{Na_2SO_4} + \underset{36{\cdot}5}{HCl}$$

On the small scale hydrochloric acid is prepared by pouring 10 parts of sulphuric acid, containing 1 part of water to 9 parts of acid, over 5 parts of common salt contained in a glass flask, fitted with a caoutchouc cork and delivery tube; the flask is heated at first gently, and afterwards more strongly, and the gas evolved is passed through a Woulfe's bottle containing a small quantity of water, so as to free it from particles of sulphuric acid carried over, and then into a bottle containing the water for the absorption of the gas for use.

When gaseous hydrochloric acid is required, it is prepared in the same way, but the Woulfe's bottle is charged with sulphuric acid instead of water, in order to dry the gas. The gas is to be collected over mercury.

The apparatus in which the operation is carried out on the large scale is of various construction, but glass retorts must be used when pure hydrochloric acid is required.

The most simple arrangement of the kind is that shown in fig. 111. It consists of four or more glass retorts placed over a single furnace. Each retort (c′) is connected with a receiver containing a small quantity of water for the absorption of hydrochloric acid. The retorts are charged by holding the neck in a vertical position and introducing the necessary quantity of common salt; they are then placed over the furnace, sulphuric acid is introduced through the bent funnel, and the neck of the retort connected with the receiver. The retorts are then heated so long as hydrochloric acid passes over.

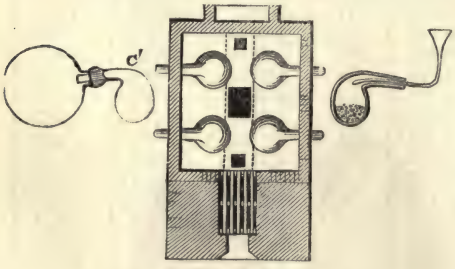


Fig. 111.

An apparatus with better arrangement for the absorption of the hydrochloric acid gas is shown in figs. 112 and 113. The glass retorts (c c) contain the mixture of salt and sulphuric acid. From four to eight of them are supported over a furnace (B), where they are heated by the hot air of the furnace (A). The retorts stand in a chamber made of fire-bricks, the hot air passing beneath and around them from the furnace flues (B′ B, B, B). A couple of furnaces of the kind, each holding 8 or 10 retorts, are so connected with one another that the fire gases escape through a common chimney, separated internally by a

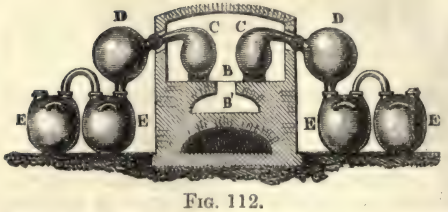


Fig. 112.

partition about 3 feet high, so as to prevent the gases from entering the chimney in opposite directions. The arrangement for condensation or absorption of the hydrochloric acid gas consists of doubly tubulated balloons (D D), into one tubulus of which the neck of the retort passes, the other being in communication with a receiver (E) below. The receivers are also furnished with a second tubulus for passing non-condensed vapours into a second or third, etc., receiver of like construction. The first receiver is at starting empty, receiving the raw hydrochloric acid as it drops from D; the other receivers contain each a small quantity of water for the effectual absorption of the hydrochloric acid vapours. The aqueous hydrochloric acid of the latter receivers is purer in quality, since the chief impurities remain in the first receiver.

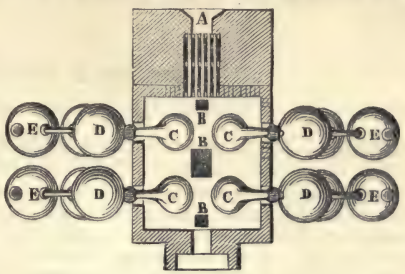


FIG. 113.

The hydrochloric acid of commerce is to some extent prepared in the manner above described; but most of the hydrochloric acid used in chemical works is obtained in making sodium sulphate from common salt, and its preparation will be treated of in the chapter describing the manufacture of that substance. (See 'Soda Manufacture.')

The saturated solution of hydrochloric acid is drawn off into glass or stoneware carboys provided with stoppers of the same material, which are either ground so that they fit accurately, or are luted into the necks of the carboys, and then covered over with a piece of strong linen. In filling the carboys for transport, it is necessary to leave in each carboy an empty space of at least a pint capacity, so as to avoid risk of breakage of the carboys in warm weather by the expansion of the hydrochloric acid.

The purification of raw hydrochloric acid may be effected in two ways—viz., either the raw acid is distilled and the product of distillation passed into water for absorption, or the raw acid is diluted till it has a specific gravity of 1·12, and then distilled. In both cases it is necessary to reject the first portion of the distillate, as it contains chlorine or sulphurous acid, or both, also to avoid distilling too far, in which case ferric chloride would distil over.

Pure hydrochloric acid may also be obtained from the raw acid, according to P. W. Hofmann, by filling a vessel furnished with doubly perforated clay plugs to one third of its capacity with raw hydrochloric acid, and then pouring through a funnel, admitting of being closed, sulphuric acid of specific gravity 1·848. This causes the immediate evolution of hydrochloric acid gas, which is passed through a sort of Woulfe's bottle containing water so as to wash it, and then collected in another vessel containing distilled water. The evolution of hydrochloric acid gas in this process is very regular, and not accompanied by any considerable rise of temperature. It ceases when the sulphuric acid has reached a specific gravity of 1·566. The residual sulphuric acid contains only 0·32 per cent. of hydrochloric acid, and may be either concentrated or used for making sodium sulphate.

For the removal of arsenic from hydrochloric acid according to Bettendorf's method, raw hydrochloric acid is mixed with a small quantity of fuming stannous chloride, the precipitate thus produced is separated after 24 hours, and the hydrochloric acid distilled off. The first tenth part of the distillate is thrown away, and the residue distilled almost to dryness. This operation serves at the same time to deprive the hydrochloric acid of chlorine.

Uses.—Hydrochloric acid is used in the preparation of the following substances:—aqua regia, which is used for dissolving gold, platinum, certain alloys, as well as minerals, etc.; stannous chloride and stannic chloride, antimonous chloride, and sal ammoniac. It is used for decomposing the lime soap formed in the bucking of linen or woollen fabrics impregnated with fat; also in bleaching instead of sulphuric acid, and for converting non-fermentable cane sugar into fermentable sugar in the manufacture of molasses spirit. Pure hydrochloric acid is also used for purifying animal charcoal; for preparing carbonic acid in the manufacture of aerated waters and double carbonates; for purifying ferruginous sand in the manufacture of glass; for removing the fur in steam boilers; in the preparation of blacking; in the preparation of copper, etc. in the wet way; for removing phosphates from iron ores; for cleansing zinc before soldering; for converting barium carbonate into chloride; also in the recovery of sulphur from soda refuse, as well as in a number of chemical operations in the laboratory.

The impure hydrochloric acid obtained as a by-product in the manufacture of soda is generally used in the manufacture of chlorine and the hypochlorites, especially bleaching powder and Javelle liquor (see p. 168). It is also used for making zinc chloride.

SULPHUR CHLORIDE.

Formula S_2Cl_2. Molecular Weight 135.

History.—This substance was first obtained by Hageman in 1782, but its constitution was not fully ascertained until it was studied by Davy and Bucholz in 1810.

Characters.—Sulphur chloride is at the ordinary temperature a mobile reddish-yellow liquid that fumes in contact with the air, and has a peculiar penetrating disagreeable smell; its specific gravity is 1·687, that of its vapour relatively to air 4·668; it boils at 139°. When brought into contact with water it gradually decomposes, and sulphur is liberated, with formation of hydrochloric acid and thiosulphuric acid, which is soon converted into sulphurous oxide and sulphur. Sulphur chloride dissolves sulphur in large proportion.

Preparation.—Sulphur chloride is prepared by passing dry chlorine gas over melted sulphur and distilling off the chloride from the excess of sulphur. The apparatus for conducting the operation is represented by fig. 114. The chlorine gas

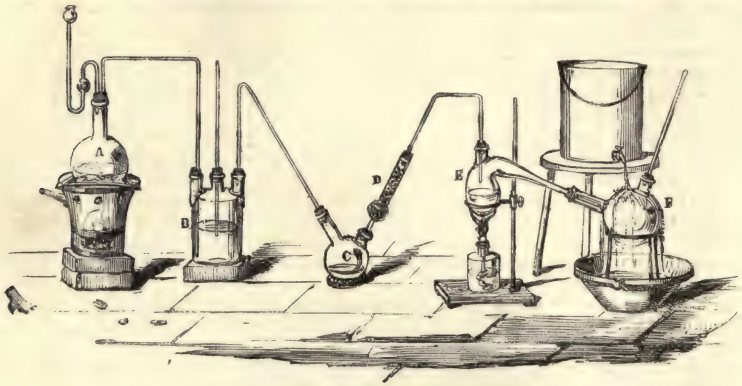


Fig. 114.

generated in the flask (A) is first washed by passing it through water in the Woulfe's bottle (B), then passed through the tubulated flask (C) and the drying tube (D), filled with calcium chloride, into the retort (E) containing the sulphur, and kept sufficiently hot by means of a spirit lamp. Combination takes place very readily, and the chloride distills over into the condenser (F), kept cold by a stream of water.

Uses.—Sulphur chloride is used as a solvent for sulphur in vulcanising caoutchouc.

BROMINE

SYMBOL Br. ATOMIC WEIGHT 80.

History.—This elementary substance was discovered in 1826 by Balard in the mother liquor obtained in the manufacture of salt from sea water, and its most important properties were ascertained by him.

Occurrence.—Bromine does not occur naturally in the free state, but in the state of combination with the alkaline metals and associated with the corresponding chlorides it occurs in sea water, in the water of salt springs, in rock salt, marine plants and animals, and also in coal. Bromides exist in considerable amount in the water of some mineral springs; for instance, that of the Adelheid spring in Upper Bavaria, in the water of the brine springs at Kreuznach, also in the water of the Dead Sea, etc. (see *ante*, p. 33). Silver bromide occurs as bromargyrite or green silver, a mineral which forms the chief constituent of some silver ores occurring in Mexico and Brittany.

Characters.—Bromine is at the ordinary temperature a dark red liquid of a penetrating and unpleasant odour. Hence its name, from *βρῶμος*, a stink. Bromine in the liquid state has a specific gravity of 2·976; at a temperature of −7·3° it solidifies as a grey mass of metallic lustre; it boils at 63°, and is converted into a yellowish-red vapour, having a density of 80 as compared with hydrogen, and relatively to air a specific gravity of 5·54. The tension of bromine at the ordinary temperature is so considerable that, when exposed to the air, it readily volatilises and gives off a red vapour resembling nitrogen peroxide in appearance. On this account bromine requires to be kept in well-stoppered glass bottles, and it is convenient to keep it covered with a layer of sulphuric acid, specific gravity 1·652, which dissolves only mere traces of bromine and prevents volatilisation. Bromine is soluble in water only to the extent of about 3 per cent. by volume, but communicates to it a reddish-yellow colour. This water solution of bromine decolorises in the sunlight, owing to the formation of hydrogen bromide by decomposition of water, oxygen being liberated. Bromine combines with water cooled down to 0°, forming a solid reddish-brown hydrate which crystallises in octahedra, and is not decomposed at a temperature of 16° to 20°. The best solvents for bromine are alcohol, ether, chloroform, aqueous solutions of potassium bromide, etc. In its chemical characters bromine closely resembles chlorine, but it has less chemical energy. Bromine does not readily combine with oxygen, but very readily with hydrogen, and the bleaching of organic substances by bromine is attributable to the facility with which it combines with hydrogen. Bromine combines with most metals, forming bromides. Starch paste yields with free bromine an orange-red compound.

Preparation.—Formerly bromine was chiefly obtained from the mother liquor of sea water, which was treated for potassium salts according to a method to be described further on. By this process, after various salts have been crystallised out, a compound of potassium chloride with magnesium chloride is obtained, in which variable quantities of chlorine are replaced by bromine. After the separation of this salt it is redissolved, and the solution evaporated to crystallisation. The greater part of the potassium chloride and magnesium chloride crystallises out, leaving behind a liquor rich in bromine, which is then mixed with manganese peroxide and sulphuric acid, and distilled from large stoneware retorts.

According to another method, the liquor from which iodine has been previously separated by chlorine is concentrated in leaden jars, chlorine having been added in small portions at a time, so long as the violet vapour of iodine is evolved. The liquor is then mixed with manganese peroxide and sulphuric acid, and the bromine distilled off; some water also passes over, and retains considerable quantities of bromine in solution. On this account the water is separated from the bromine by means of a separating funnel or by decantation, treated with potassium carbonate, evaporated, and

calcined. The residue contains the whole of the bromine that was dissolved in the water as potassium bromide, and it is distilled with manganese peroxide and sulphuric acid.

The manufacture of bromine at Stassfurt was started by Frank, in 1865, at a time when bromine had become very dear. The result was that, in 1866, the price of bromine was reduced one-half, in 1867 to one-fifth, and still further during the years 1868, 1869, and 1870. The production was at first 3,000 pounds per annum; it soon rose to 15,000 pounds, and has since then increased considerably.

The raw material employed by Frank in the preparation of bromine is the mother liquor which remains after separating potassium chloride and the double potassium and magnesium chloride from the solution of raw Stassfurt salt by crystallisation (*vide* Potassium Salts). This liquor contains from 1 to 1·5 per cent. of potassium chloride, 30 to 33 per cent. of magnesium chloride, 1 to 1·5 per cent. of sodium chloride, 1 per cent. calcium chloride, the remainder consisting of water. It also contains about 0·08 or 0·15 per cent. of bromine. The amount of bromine varies considerably, and the more recent of the salt deposits, especially those containing tachhydrite, are richer in bromine than the others.

The apparatus used in distilling bromine consists of a stoneware pan, set in brickwork, having a capacity of about 80 to 100 cubic feet. It has essentially the same construction as the chlorine generator, described on page 165, the only difference being that it is heated with steam. For this purpose a leaden steam pipe passes through the lid of the still to the bottom, so as to deliver jets of steam from several

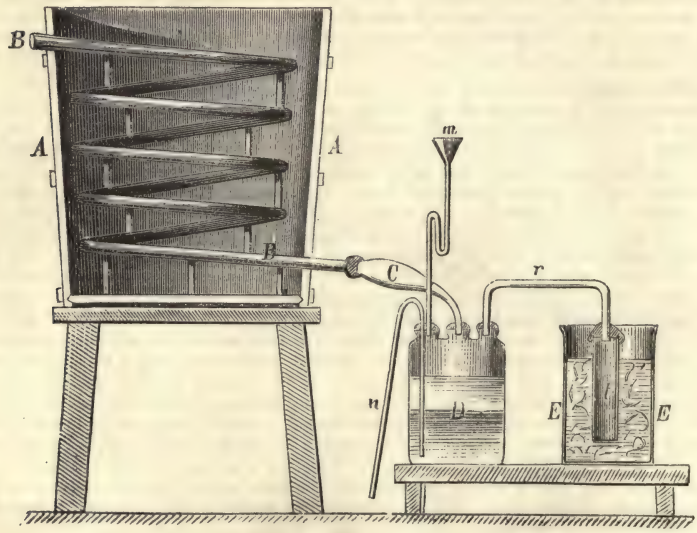


FIG. 115.

places. The delivery tube of the still is connected with a condensing worm (B B, fig. 115) of earthenware or lead, surrounded by cold water, and the end of the worm is connected by means of a glass adapter (C) with a three-necked Woulfe's bottle (D) holding about 18 pints, and fitted with a safety funnel (*m*) and a siphon (*n*) for drawing off the bromine. A leaden tube (*r*) connects D with a stone jar (E), filled with moist iron filings. The end of the tube (*r*) terminates in a wide glass cylinder (*t*), to prevent stoppage of the narrow leaden tube by the formation of ferrous bromide. The joints are made with a lute of clay and oil bound round with parchment.

The apparatus is set going by charging the still with mother liquor, manganese peroxide, and sulphuric acid, or hydrochloric acid, and heating the mixture as quickly as possible to the boiling point by passing steam into the still.

The escaping vapour condenses in the worm, and passes through the adapter (C) into the Woulfe's bottle (D), where two layers are formed, the lower layer consisting of bromine, the upper one of a solution of bromine in water. The uncondensed vapour, which is very offensive owing to the bromine it contains, passes into (E E), and is there completely absorbed by the moist iron filings. At the beginning of the operation

tolerably pure bromine passes over, but towards the end of the distillation the evolution of chlorine increases, as may be seen by the green colour of the vapour in the adapter (c). Directly this is the case the distillation is stopped and the generator emptied.

Purification.—The bromine which collects in the Woulfe's bottle is contaminated with chlorine, with brominated hydrocarbon compounds not as yet studied, as well as with lead bromide carried over from the leaden worm and the leaden delivery tube. It is therefore drawn off by means of the siphon and submitted to a process of rectification. The apparatus for the rectification consists of large tubulated glass retorts, the necks of which are luted into receivers also of glass. The tubulus of each receiver is furnished with a glass tube fitted tightly into it, through which the uncondensed vapour passes for absorption into a Woulfe's bottle filled with potash or caustic soda solution, then into an open pot containing the same absorbent, or moist iron filings may be employed instead of caustic alkali. The retorts are heated in sand baths, consisting of a single casting, and they have double sides between which steam is passed. When the retorts have been arranged as above described, they are charged with crude bromine and heat applied. The first portion of distillate consists of bromine considerably contaminated with chlorine, which is collected separately, mixed with other products of the same nature, and again rectified. If the first portion of distillate happens to be pure bromine chloride, it is treated with water, which causes the decomposition of the compound into bromine and hydrochloric acid. After the first chlorinated portion of distillate has been removed, and pure bromine distils over, the receivers are changed and the pure bromine collected. There remains in the retort, when the distillation is over, a thick dark mass, consisting of various lead salts and brominated hydrocarbon compounds.

Packing.—The bromine is run off from the receivers into glass vessels furnished near the bottom with glass cocks, through which the bromine is run into the bottles for transportation, which hold from 4 to 5 pounds of bromine, and are closed with well-ground glass stoppers, covered with resin, over which is a clay luting secured with parchment paper; four such bottles being packed in a box with four compartments.

For the transport of bromine by sea, Frank evaporates a solution of ferrous bromide to dryness, and packs the thoroughly dried mass in bottles. When required for use this mass is dissolved in water, and the bromine separated by passing chlorine into the solution. This method avoids the danger of leakage from an ill-fitting stopper or loss by the breaking of bottles.

The bromine obtained from Stassfurt has the advantage over all other kinds of commercial bromine, that it is entirely free from iodine.

Uses.—Bromine in the form of potassium bromide is used extensively in photography and also in medicine. The use of bromine in the preparation of aniline colours, which at one time seemed likely to be extensive, has nearly ceased. Bromine also enjoys repute as a disinfectant.

Compounds.—Bromine closely resembles chlorine in its chemical relations, and the bromides or compounds it forms with other elementary substances have a general analogy to the corresponding compounds of chlorine in constitution and characters. The hydrogen compound HBr, or hydrobromic acid, is a colourless gas soluble in water; it is decomposed by chlorine with liberation of bromine and formation of hydrochloric acid. The metallic bromides are in like manner decomposed by chlorine and converted into chlorides with liberation of bromine; they are also decomposed by hydrochloric acid with formation of chlorides and hydrobromic acid. Bromine appears to combine with chlorine, forming a substance which is probably a pentachloride, $BrCl_5$.

The oxygen compounds of bromine correspond to hypochlorous oxide and chloric, but they are known only in combination with water or basic oxides. These compounds resemble the corresponding compounds of chlorine, and are formed in the same manner; thus hypobromites are formed by digesting bromine in cold solutions of the caustic alkalies or alkaline earths. Bromates are formed together with bromides either by boiling a solution of hypobromite or by saturating hot alkaline solutions with bromine, the reaction being precisely similar to that which takes place in the formation of chlorates:

$$6KHO + 6Br = 5KBr + KBrO_3 + 3H_2O.$$

IODINE.

Symbol I. Atomic Weight 127.

History.—This elementary substance was discovered in 1811 by Courtois in varec soda, and it was immediately made the subject of research by Clément and by Gay-Lussac, who was the first to express the opinion that iodine was to be regarded as an element very nearly related to chlorine. Davy also studied iodine, and ascertained that when it is acted upon by caustic potash solution, it is oxidised, with formation of potassium iodate. The reaction of iodine with starch, which is reciprocally one of the most delicate tests for both iodine and starch, was discovered by Colin and Gaultier de Claubry.

Occurrence.—Iodine does not occur naturally in a free state, and in a state of chemical combination it occurs chiefly as potassium iodide and sodium iodide in sea water. The amount of iodine in sea water is, however, relatively so small, that its presence can only be determined with difficulty. It occurs in larger proportion in some kinds of fuci, algæ, and other marine plants, which extract iodine from sea water and store it up in their tissues. Iodine has also been found in marine animals, such as sponges, star-fish, and the like.

Iodine exists, probably in the state of iodides, in the water of most brine springs, but not generally in sufficient amount to admit of its presence being easily ascertained, except in the mother liquor obtained by evaporating large quantities of water.

Iodine is found in relatively greater amount, also in combination with potassium and sodium, in the water of some mineral springs, as, for instance, in the Adelheid spring in Bavaria, and in the water of Hall, in Austria. Iodine has also been found in a number of minerals, in some Silesian zinc ores, in a silver ore from Mexico, in the phosphorite of Amberg, in turf, and in the coal of Mons, Anzin, Comentry, etc., which is used in gas-making. Chili saltpetre also contains a considerable amount of iodine, which is found in the mother liquor obtained in purifying this salt.

Characters.—Iodine is at the ordinary temperature solid, either presenting the appearance of a compact mass with crystalline fracture or well-defined crystals. It has a metallic appearance, is opaque, and of a greyish black colour. Its specific gravity is 4·950 at 15°; it melts at 107°, forming a black liquid, which boils at 180°, yielding a beautiful violet coloured vapour, the specific gravity of which is 8·716, as compared with air and its density 127 times that of hydrogen. The name this element bears is in allusion to this character, being derived from *ἰώδης*. violet-like.

The tension of iodine at the ordinary temperature is great enough to cause the volatilisation of small quantities of the substance, and its penetrating smell, as well as the corrosion of cork or other organic substances used for securing bottles containing iodine, are due to this fact. At a temperature of from 45° to 50° the evaporation of iodine is so considerable, that the upper part of bottles partly containing iodine are filled with the violet vapour. When water containing iodine in solution is boiled, iodine passes over with the steam in considerable quantities. Dry iodine vapour deposits crystals of iodine upon cold surfaces. Very good crystals may also be obtained from solutions of iodine in potassium iodide, carbon bisulphide, etc. Iodine precipitated from its alcoholic solution, by the addition of water, is found, when examined under the microscope, to consist of a conglomerate of small crystals. Iodine has an acrid taste, and it acts very energetically upon the animal organism.

Iodine is but slightly soluble in water, requiring for its solution 5,524 times its weight of water; such a solution has a brownish colour. It is easily soluble in aqueous solutions of hydriodic acid, or potassium iodide, and, generally speaking, iodine is far more soluble in water containing salts than in pure water. The best solvents for iodine are carbon bisulphide, alcohol, ether, ethyl iodide, chloroform, etc. Iodine is not very readily oxidisable, but combines much more readily with hydrogen;

though in this respect it is surpassed by chlorine as well as by bromine. Iodine combines directly and readily with sulphur and phosphorus; it combines also with the metals to form metallic iodides. It dissolves in solutions of the caustic alkalies, forming iodide as well as iodate of the metal.

Tests for Iodine.—Pure, refined iodine ought to volatilise completely when heated to 180°; it should dissolve in alcohol without leaving a residue, and the solution ought to be completely decolorised when treated with an excess of caustic soda or potash solution.

Iodine in an uncombined condition produces an intensely blue colour with starch, and in testing for the presence of iodine it is usual to employ either freshly prepared starch paste, or papers smeared with such paste and dried. If the iodine be in combination, this colour does not appear until a drop of some oxidising agent such as chlorine water, fuming nitric acid, or potassium nitrite, has been added to set the iodine free.

Another way of ascertaining the presence of iodine is by shaking up a liquid containing free iodine with carbon bisulphide, which extracts the iodine and forms a red liquid easily discernible at the bottom of the test tube, after allowing the mixture a short time to settle.

Commercial iodine is often adulterated with coal, charcoal, or graphite; but these adulterations are easily recognised by treating the iodine with alcohol, in which pure iodine dissolves, while the admixtures remain unacted upon.

Preparation.—Iodine is prepared chiefly from the mother liquors obtained after separating potassium chloride and other salts from the ashes of seaweed, known in this country as kelp, and in France by the name of varec.

According to Courtois' method, as improved by Wollaston, the alkaline iodides contained in the mother liquor are decomposed by sulphuric acid and manganese peroxide, care being taken that these materials are not added in very great excess, since in such cases chlorine and iodine chloride are formed. The reaction which takes place is represented by the following equation:—

$$2KI + 2H_2SO_4 + MnO_2 = K_2SO_4 + MnSO_4 + 2H_2O + 2I.$$

The liquor is first mixed with sulphuric acid in large vessels, in such a way that as little increase of temperature as possible takes place. By this means sulphates of the alkalies are produced, together with hydriodic acid, hydrochloric acid, sulphuretted hydrogen, and carbonic acid, while sulphur is separated in the free state, and is removed with a perforated ladle. Of the acids thus produced, only carbonic and hydrosulphuric acids escape, while hydriodic and hydrochloric acids remain dissolved. The mixture is allowed to remain at rest, until it ceases to smell of sulphuretted hydrogen; it is then drawn off from the precipitated sulphates, and placed in a still with manganese peroxide. The arrangement of the distilling apparatus is represented by fig. 116; it consists of a cylindrical leaden vessel (*a*) furnished with a head, and placed in communication with a number of glass or stoneware receivers (*d*). The still is heated over a sand bath, the temperature being gradually increased until violet vapour of iodine is given off, which condenses in the receivers, and is deposited there in the form of a crystalline crust. The stoppered neck (*b*) in the head of the still serves for introducing the charge, and the smaller aperture (*c*) for ascertaining the progress of the operation.

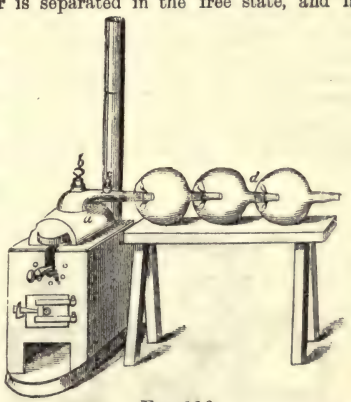


FIG. 116.

Mr. Paterson, in Glasgow, distils from hemispherical vessels of cast iron 4 feet wide, and furnished with a leaden head. The latter is closed above with a round clay plate, furnished with an opening for admitting the manganese peroxide, and two openings for the escape of the iodine vapours into two rows of receivers. The manganese peroxide is added in small portions at a time. Five sets of stills of this kind are placed side by side, each being heated by a separate furnace.

According to Barruel's method, the iodine is separated by means of chlorine. At Cournerie's works, in Cherbourg, the liquor, saturated exactly with sulphuric acid, is mixed with 10 per cent. of manganese peroxide and evaporated. In this way the

sulphides and hyposulphites are oxidised to sulphates; and the residue is heated until iodine vapour appears. The completion of the oxidation may be ascertained by mixing a small quantity of the mass with water in a test tube, and adding sulphuric acid, which does not cause any evolution of sulphuretted hydrogen if the oxidation is complete. The calcined mass prepared as above is then treated with water, and the solution brought to a specific gravity of 1·333. After it has become clear by standing, the clear portion is decanted off, diluted with water to specific gravity 1·197, and accurately saturated with chlorine gas. This causes the decomposition of the alkaline iodides into free iodine and chloride of the metal according to the equation:

$$KI + Cl = KCl + I.$$

The chlorine is generated in the apparatus described on page 165, fig. 103. Care must be taken that exactly the right proportion of chlorine is employed; it ought neither to be insufficient in quantity nor in excess. In the latter case iodic acid and iodine chloride are apt to be formed; while in the former case the iodine is not all separated, and the undecomposed potassium iodide retains a further quantity of iodine dissolved, so that in either case there is a loss of iodine. In order to ascertain whether the proper quantity of chlorine has been introduced, two portions of the liquor are tested respectively with chlorine water and with solution of potassium iodide. In neither case ought a separation of free iodine to take place. When this point has been attained, the liquor is allowed to settle, so that the iodine may deposit, the supernatant liquor is decanted off, and the residual iodine washed with cold water until nothing more is dissolved. The washed iodine is placed upon a sieve and drained. In order to dry it as far as possible, it is either spread out upon filter paper laid upon dry ashes, or it is laid upon plates of porous earthenware. The iodine is sometimes dried by passing over it a current of air at a temperature of about 25°. Frequently, however, it is not dried at all; and the adherent water is separated from it in the process of sublimation.

A number of propositions have been made for the separation of iodine from kelp liquor. Wagner, for instance, suggests distilling the liquor, previously acidulated with sulphuric acid, with ferric chloride, which gives rise to the following reaction:—

$$2NaI + Fe_2Cl_6 = 2I + 2NaCl + 2FeCl_2.$$

This method has the advantage that no formation of iodine chloride is possible. Luchs recommends treating the liquor with sulphuric acid and potassium chromate. Soubeiran obtained iodine from liquor poor in that substance by precipitation as cuprous iodide, by adding ferrous sulphate and cupric sulphate, and then decomposing the cuprous iodide with manganese peroxide and sulphuric acid to liberate the iodine. Theroulde separates the iodine by means of nitrous acid. An analogous process is that of Lauroy, in which the nitrous acid is converted into nitrogen peroxide by mixing it with air before passing it into the liquor.

Sublimation of Iodine.—Before iodine is sent into the market, it is refined by sublimation, in order to free it from adherent moisture. The apparatus commonly used is shown in fig. 117. It consists of six stoneware retorts (A A), resting upon a sand bath (B B), and surrounded entirely by sand. The necks of the retorts pass through the side of the sand bath, and the ends of them fit accurately into large stoneware receivers (D D). The necks of the retorts must be as short as possible, to avoid the deposition of iodine within them. The receivers are furnished with a tubulus (*f*), into which is fitted a tube (*g*), for the escape of air. Each receiver has a lid (*e*) above, for the removal of the iodine; and near the bottom is a perforated plate for the escape of condensed water. The entire number of retorts are heated by the fire (C). Each retort is charged with about 40 pounds of iodine, and is heated so long as iodine vapour escapes into the receivers. The iodine deposits in the receivers in crystalline laminæ. In Cournerie's iodine works the retorts are heated in a solution of salt instead of the sand bath.

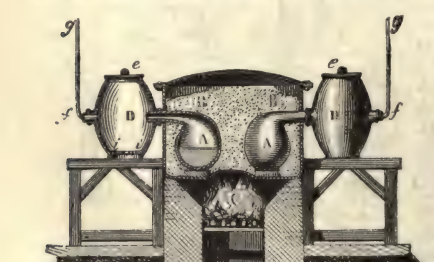


Fig. 117.

Extraction of Iodine from Chili Saltpetre.—The mother liquor obtained in

refining Chili saltpetre is so rich in iodine that it is now usual to treat it for iodine. At Tarapaca, in Peru, the liquors containing iodine were formerly treated with sulphuric acid, by which iodic acid is reduced; but this method gives rise to a number of inconvenient by-products, such as sodium sulphate, which renders the saltpetre impure, and hygroscopic substances which adhere to the iodine. Thiercelin has therefore introduced a new method of reducing the iodic acid by means of nitrous acid, obtained by heating to redness a mixture of 1 part charcoal and 5 parts of saltpetre, in a manner similar to that adopted in the preparation of sodium carbonate. The iodine is thus precipitated in a form which admits of its being easily washed and dried, and the precipitate contains about 80 per cent. of iodine.

For the determination of the value of commercial iodine Hesse's method is the best. For this purpose a solution of ammonium sulphite is made by saturating a 4 per cent. solution of ammonia with sulphurous acid. A weighed quantity of iodine is dissolved in this ammonium sulphite solution, and thus converted into hydriodic acid:

$$\underset{116}{2NH_4,SO_3} + \underset{18}{H_2O} + \underset{254}{2I} = \underset{132}{2NH_4,SO_4} + \underset{256}{2HI}$$

The hydriodic acid is decomposed with silver nitrate, the precipitated silver iodide filtered off, washed with water, dried and weighed. The amount of iodine is estimated from the weight of the silver iodide. When chlorine is present, silver chloride is also precipitated, and hence the quantity of iodine found would be in excess of the real amount. In order to remove this source of error, the precipitated silver iodide, before being dried and weighed, is treated with concentrated aqueous ammonia, which dissolves silver chloride, leaving the silver iodide intact. The silver chloride held in solution by ammonia is then precipitated by adding nitric acid, its weight determined, and from the latter the amount of chlorine and iodine chloride calculated. By subtracting the amount of iodine which was present in the form of iodine chloride from the total amount of iodine found, the weight of free iodine present is obtained.

Use.—Iodine is used in considerable quantity in medicine; and in making a number of pharmaceutical preparations, such as potassium iodide, mercurous iodide, and mercuric iodide, etc. Mercuric iodide is further used as a red pigment. However, the greatest consumption of iodine is in photography, in the form of potassium iodide. Iodine is also used for producing certain aniline dyes. It is finally a very important and necessary substance in many chemical analyses and other operations of the laboratory.

Compounds.—Iodine resembles chlorine and bromine in its chemical relations and compounds. The hydrogen compound HI, or hydriodic acid, is a colourless gas soluble in water; it is decomposed by chlorine and by bromine with formation of hydrochloric or hydrobromic acid and liberation of iodine. The iodides are decomposed in the same way, and by hydrochloric or hydrobromic acid, with formation of hydriodic acid and chlorides or bromides. Some of the metallic iodides are remarkable for their brilliant colours, but in most other respects they have a general analogy with the chlorides and bromides.

Iodine combines with chlorine in two proportions, forming a monochloride ICl, and a terchloride ICl_3; it also forms with bromine a monobromide IBr, and another compound, probably IBr_5.

The oxygen compounds of iodine that are known are iodic oxide I_2O_5 and I_2O_7, both of which combine with water and basic oxides, forming saline compounds, respectively termed iodates and periodates, the hydrogen salts being iodic acid HIO_3, and periodic acid HIO_4. The iodates correspond generally with the chlorates and bromates, and are formed in the same manner. The periodates correspond with perchlorates.

FLUORINE.

SYMBOL F. ATOMIC WEIGHT 19.

History.—The analogy between hydrochloric acid and the acid obtained by decomposing fluorspar with sulphuric acid was first suggested in 1810 by Ampère, who, on this ground, assumed the existence of an elementary substance similar to chlorine, and regarded the acid obtained from fluorspar as being a hydrogen compound. This view was more fully established by Sir H. Davy, J. Davy, and Berzelius, between 1812 and 1823.

The name fluorine was applied to this substance as indicative of its being a constituent of fluor spar, so called from the Latin word *fluo*, on account of its efficacy as a flux in promoting the fusion of certain minerals, etc.

Occurrence.—Fluorine occurs only in a state of combination, chiefly with calcium as fluor spar; also combined with aluminum and sodium as cryolite, with aluminum and silicon in topaz, and with cerium and yttrium in fluocerite and yttrocerite. In smaller amounts fluorine occurs as calcium fluoride in apatite, and in other forms of combination in wavellite, wagnerite, and a number of other minerals. Bones both fossil and recent contain traces of fluorine, and in very minute proportions it occurs in the water of some mineral springs and rivers, as well as in certain plants.

Characters.—Although the probability that this constituent of the mineral known as fluor spar is an elementary substance is now tolerably beyond question, and though its analogy in this respect with chlorine, bromine, and iodine has been for some time established by the study of its various compounds by Davy and Berzelius, little is yet known of the characters of fluorine in a free state; for, on account of its powerful action upon almost all materials ordinarily used for constructing chemical apparatus, it is doubtful whether fluorine has ever been isolated, and certainly it has never been obtained in such a condition that its characters could be determined.

Compounds.—The substances consisting of fluorine in combination with some other elementary substance are termed fluorides, and are analogous in constitution to the chlorides, bromides and iodides. Most of these salts are solid substances, and are not decomposed when heated in a dry state; but many of the fluorides containing metals are readily fusible and some of them are volatile; the hydrogen compound HF, known as hydrofluoric acid, is gaseous; the compounds of fluorine with silicon SiF_4 and with boron BF_3 are also gaseous.

The alkaline fluorides are soluble in water and crystallisable; those of the earthy metals are almost insoluble; but several of the metallic fluorides, for instance, the tin and silver salts, are readily soluble in water, and hydrofluoric acid dissolves in about twice its weight of water.

Many of the fluorides combine together, forming definite crystallisable double salts; thus potassium fluoride combines with hydrofluoric acid, forming a crystallisable salt the composition of which is KF,HF. This capability is very characteristic of the fluorides, and a number of similar salts are known, among which the sodium-aluminum fluoride, $3NaF,AlF_3$, occurs naturally as cryolite.

Silicon fluoride combines with hydrofluoric acid or with metallic fluorides, forming compounds called fluosilicates or silicofluorides; the composition of the hydrogen compound, fluosilicic acid, is represented by the formula H_2SiF_6. The same substance is formed, together with silica, when silicon fluoride is decomposed by water, as shown by the following equation:

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6.$$

Potassium fluoride also combines with silicon fluoride, forming potassium fluosilicate, a salt corresponding to the hydrogen compound fluosilicic acid, and represented by the formula $2KF,SiF_4$, or K_2SiF_6. These compounds correspond to ordinary silicates, six

atomic proportions of the monovalent element fluorine taking the place of three atomic proportions of the divalent element oxygen.

Similar compounds are formed, together with water, when silica or silicates are acted upon by hydrofluoric acid; thus calcium silicate yields

$$CaSiO_3 + 6HF = CaSiF_6 + 3H_2O.$$

The fluosilicates are mostly soluble in water, but the potassium and barium salts are very sparingly soluble.

Boron fluoride BF_3, stannic fluoride SnF_4, and titanic fluoride TiF_4, form with hydrofluoric acid and with the metallic fluorides similar compounds, which are called borofluorides or fluoborates, fluostannates, and fluotitanates, salts corresponding to borates, stannates, and titanates in the same manner that the fluosilicates are related to silicates, by containing fluorine in the place of oxygen.

HYDROFLUORIC ACID.

Formula HF. Molecular Weight 20.

History.—The corrosive action exercised upon glass by a mixture of fluor spar and sulphuric acid was known as long since as 1670, and it was probably turned to practical account for etching glass in 1725; but nothing definite was then known of the substance to which this effect was due; and though Scheele suggested that it was a peculiar acid existing in fluor spar in combination with lime, the corrosion of the vessels used in preparing the acid prevented its true character from being recognised, until Ampère suggested that the constitution of this acid was analogous to that of hydrochloric acid, and this view was soon afterwards confirmed by Davy and Berzelius.

Characters.—Hydrofluoric acid is a colourless gas which forms dense irritating fumes in contact with moist air, and is copiously absorbed by water. It condenses at $-28°$ to a thin liquid, having a specific gravity of ·988, and boiling at 19°·4. When quite dry it does not act upon glass or upon most metals; but when moist it reacts violently with potassium or sodium; mixed with water, it evolves great heat and forms a solution which has a specific gravity of 1·06 and is very caustic, producing painful ulcers on the skin. It dissolves metals, forming fluorides, with evolution of hydrogen; it also dissolves silicon, forming silicon fluoride SiF_4, which combines with another portion of the hydrofluoric acid, forming fluosilicic acid H_2SiF_6. Silica and silicates are also readily dissolved by hydrofluoric acid, forming silicon fluoride, metallic fluorides, and water.

Preparation.—Hydrofluoric acid is prepared by gently heating a mixture of fluor spar and concentrated sulphuric acid. The reaction taking place is represented by the following equation:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

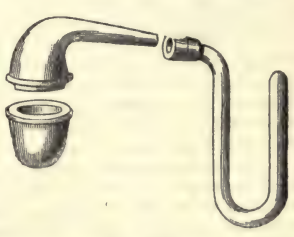


Fig. 118.

A strong solution of the acid is now prepared for etching glass by distilling a mixture of powdered fluor spar with twice its weight of concentrated sulphuric acid, in a leaden retort constructed in the manner represented by fig. 118. The acid is condensed in the leaden tube fitted to the beak of the retort and surrounded by a freezing mixture.

Uses.—Hydrofluoric acid is used for etching glass, and as a solvent in the analysis of silicates.

In both cases the gaseous acid is often used, and the substance to be acted upon is suspended in an atmosphere of the gas generated from a mixture of fluor spar and sulphuric acid, in a suitable leaden chamber; when silicates are decomposed in this way for analysis, platinum vessels must be used.

In etching glass it is first coated with a thin layer of wax, and the design traced in the wax so as to expose the glass where the action of the acid is required.

BORON.

SYMBOL B. ATOMIC WEIGHT 11

History.—This elementary substance was isolated by Gay-Lussac and Thenard in 1808 and almost at the same time by Davy.

Occurrence.—Boron does not occur naturally in the free state, but only in combination with oxygen and hydrogen as sassolin, or with oxygen and various basic oxides in the form of borates, as in tincal, boracite, hydroboracite, and datolite; in smaller amount it also occurs in tourmaline and some other minerals.

Characters.—Boron is a solid substance capable of assuming two distinct modifications—amorphous and crystalline. In the amorphous state it is a dark greenish brown powder, destitute of taste or smell; it is very slightly soluble in water, to which it gives a slight colour, and it stains the skin brown. At the ordinary temperature it does not oxidise by exposure to atmospheric air; when heated it does not melt or sublime, but at about 300° it takes fire when in contact with air and burns with a reddish light, forming boric oxide B_2O_3.

Crystalline boron presents the form of octahedrons of a yellow or reddish colour with considerable lustre, hardness, and refractive power; the specific gravity is 2·63. In this state boron is oxidised only at a very high temperature, and is not acted upon by acids or solutions of caustic alkalies, but in the amorphous condition boron is oxidised by nitric acid or sulphuric acid.

Compounds.—Boron is a trivalent element, and its compounds with fluorine, chlorine, bromine, oxygen, and sulphur have the formulæ BF_3, BCl_3, BBr_3, B_2O_3, B_2S_3. The most important compounds of boron are the oxide B_2O_3, and the saline substances it forms with basic oxides, which are known as borates, the compound with water $B_2O_3 3H_2O$, or the hydrogen salt H_3BO_3, being termed boracic acid.

The borates corresponding in composition to boracic acid, and containing three atomic proportions of a monovalent element or corresponding proportions of polyvalent elements, to one atomic proportion of boron, are probably the normal or neutral salts; but many of the borates contain larger proportions of boric oxide, thus ordinary sodium borate in the anhydrous state contains two molecules of boric oxide combined with one molecule of soda, and is represented by the formula $Na_2O,2B_2O_3$.

The borates containing boric oxide and oxides of monovalent or divalent metals in equal molecular proportions are termed metaborates, and they are often represented according to the formula MBO_2; thus the salt obtained by melting together sodium carbonate and boric oxide in molecular proportions has in the anhydrous state a composition corresponding to the formula $Na_2O,B_2O_3 = 2NaBO_2$; in the hydrated state this salt contains four molecules of water, and may be represented by the formula $NaBO_2 + 4H_2O$, or as $\left\{\begin{matrix}Na\\H_2\end{matrix}\right\} BO_3 + 3H_2O$. Borates containing excess of boric oxide may be represented as compounds of a metaborate with boric oxide, and according to this view ordinary sodium borate would be $2NaBO_2 + B_2O_3$.

Boric oxide is formed when boron is burnt in oxygen gas, or when the hydrated oxide, boracic acid, is heated to redness and its water separated. The melted boric oxide solidifies on cooling to a brittle glassy mass, which has a slight bitter taste, and dissolves slowly in water, forming boracic acid by combination with a portion of the water; it also dissolves in alcohol, and renders the flame of the alcohol green. Boric oxide does not sensibly volatilise when heated; melted with basic oxides, it unites with them, forming borates; and at a high temperature it displaces other acid oxides from a great number of salts, combining with the basic oxides to form borates.

Boric oxide occurs in a number of minerals in the form of borates: as boracite (magnesium borate and magnesium chloride), as boronatrocalcite (sodium borate with calcium borate), as hydroboracite (calcium and magnesium borate), as lagonite (iron borate), as larderellite (ammonium borate).

Many of the compounds of boric oxide with basic oxides are but sparingly soluble in water, but the alkaline borates dissolve readily in water, and though they are acid

salts, the solutions colour litmus wine-red or even blue when they are dilute. The most important of the borates is the acid sodium salt $Na_2O2B_2O_3 + 10H_2O$, which occurs naturally in the water of certain lakes in Persia, India, and other parts of Asia, and is known under the name of tincal and magnesium borate or boracite.

BORACIC ACID.

FORMULA H_3BO_3. MOLECULAR WEIGHT 62.

History.—The first mention of boracic acid is by Becher in 1674, who described it as a 'volatile salt' obtained by heating together oil of vitriol and borax. The preparation of this substance was first described with accuracy in 1702 by Homberg. Stahl and Lemery gave new methods of preparing boracic acid, and its composition was determined by Gay-Lussac, Thenard, Davy, and Berzelius.

Formerly the only source of boracic acid known was the tincal coming from Asia; but in 1777 Höfer found it in the lagoons of Monte Rotondo in Tuscany, and in 1788 Westrumb determined its presence in boracite. Boracic acid was not employed industrially until 1776.

Occurrence.—Boracic acid occurs naturally as sassolin in volcanic districts together with sulphur. In the Lipari Islands and some parts of Tuscany, large quantities of boracic acid are brought up to the surface of the earth, together with steam. These vapour springs, called suffioni or fumaroles, form marshes and lakes, and the boracic acid is held in solution by the condensed water.

The formation of boracic acid in the interior of the earth has been the subject of much speculation. Dumas ascribes it to the action of sea water upon boron sulphide, sulphuretted hydrogen being formed at the same time. Bolley supposes it to be produced by the action of ammonium chloride vapour upon borates; R. Wagner and Warington suggest that boracic acid may be formed together with ammonia by the decomposition of boron nitride by water. Bischof considers that boracic acid is liberated in the interior of the earth by the action of superheated steam upon minerals containing the acid, especially turmalin.

The fumarole vapour contains, according to Payen, finely divided solid substances mechanically suspended, such as calcium, magnesium, ammonium and iron sulphates, manganous sulphate, alumina, hydrochloric acid, organic substances, clay, sand, a small quantity of boracic acid, and a peculiar volatile oil. The gaseous constituents vary, as may be seen from the following table:

	I.	II.	III.
Sulphuretted hydrogen	4·1	3·7	85·1
Carbonic acid	91·6	90·7	
Oxygen	0·	0·	2·7
Nitrogen and combustible gases	4·3	5·6	12·2
	100	100	100

The unabsorbable gas consists, according to Payen, of—

Nitrogen	43·35
Hydrogen	28·56
Marsh gas	28·09
	100

Leblanc and Deville found the fumarole vapour to contain 93·6 per cent. carbonic acid and 6·4 per cent. sulphuretted hydrogen.

Characters.—The boracic acid of commerce forms white scaly, shining crystals, which on heating give up the entire amount of water contained in them, melting to a transparent mass, which solidifies on cooling to a colourless glass. Boracic acid is not very soluble in water, requiring for its solution 25·6 parts of water at 15°, but only 2·9 parts at 100°. It is also soluble in alcohol and wood spirit, and these solutions burn with a green flame when ignited. The aqueous solution of boracic acid has only a very slight acid taste; it colours blue litmus paper purple, and turmeric paper reddish brown. Although aqueous boracic acid is but a weak acid, boric anhydride expels at a red heat nearly all other acids, even the strongest, from their compounds. Upon distilling an aqueous solution of boracic acid, considerable quantities of the acid pass over with the steam.

Preparation.—Most of the boracic acid of commerce is obtained from the suffioni or fumaroles of Tuscany.

To obtain the boracic acid the suffioni are surrounded with basins of rough masonry, called lagoons, several of which are arranged in steps one above the other (A, B, C, D, E, F, G, H, figs. 119 and 120). The contents of the first basin pass through the tubes (*a*, *b*, *c*) into the basin next below it, and from thence into a still lower one, etc.



FIG. 119.

Fresh water from a neighbouring spring is conducted into the uppermost basin, while gases and vapours from the fumaroles rise through this water from beneath, their action being often violent enough to cause the ejection of the water contained in the basins to a height of several feet. After the lapse of 24 hours the liquor in the first basin is generally muddy and is then conducted through *b* into the second basin (C D), the first basin being recharged with fresh water. After another lapse of 24 hours the contents of the second basin (C D) are passed into the third basin (E F), the contents of the first into the second, and so on, until the liquid has passed through four or five basins. From the last lagoon (G H, fig. 120) the solution passes into the three rectangular reservoirs (I J K, figs. 120 and 121), where it deposits solid earthy constituents. It is then decanted and brought into the evaporating pans (L, M, N, O, P, Q, fig. 120), which are placed in couples, one above the other. These pans are heated by the gases and vapours of fumaroles that on account of their situation admit of no other utilisation. For this purpose such fumaroles are enclosed with woodwork, and their vapours conducted in brick flues under the evaporating pans. The condensed water collects at the bottom of the flue, and the uncondensed gas and vapour escape from beneath the uppermost pan into the air. The evaporating pans are square, about a foot deep and 9 feet square; they are supported on wooden beams. The solution decanted from the last reservoir (K) is distributed in the first eight pans (L L, M M, N N, O O) and heated for 24 hours. When the solution has attained a density of 1·017 it is again decanted into the pans (P P, Q Q) in which it remains another 24 hours, and is concentrated to 1·034, and is then finally evaporated in the last four pans to a sp. gr. of 1·070. The temperature of the solution gradually increases on its passage, being in the first pans about 60–71° C., in the following pans about 75° C., and in the last pans the temperature is as high as 80° C. In all these pans a precipitation of gypsum takes place, which requires to be removed from time to time. The solution contained in the last four pans having a sp. gr. of 1·070, is run through the funnels (R R, figs. 120 and 121) into the crystallising vats (S S, figs. 120, 121 and 122) consisting of wooden tubs lined with lead. The crystallisation is complete at the end of 24 hours; the mother liquor is then

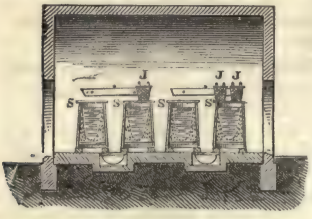


FIG. 122.

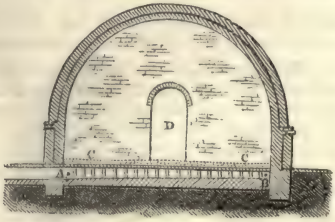


FIG. 123.

decanted off and distributed through the four evaporating pans (P P, Q Q) a few hours before the termination of a concentrating operation. The crystals are drained in the baskets

(J J, fig. 122), and after 24 hours they are spread out upon the bottom of a large drying oven (C C, fig. 123). The heating of this oven is likewise effected by the vapour from the fumaroles, which is led under the bottom of the oven in the direction from A to B. The layer of boracic acid, generally about two or three inches thick, is stirred at intervals, so as to assist the drying, which is complete at the end of 24 hours. An apparatus of the above kind yields at each operation about 200 lbs. of boracic acid.

At the present time there are ten boracic acid works in operation, viz. at Monte Cerboli, Larderello, San Federigo, Castel Nuovo, Sarro, Monte Rotondo, Lustignano, Serranzano, Lago and San Eduardo. Each of these works has from 8 to 35 lagoons, 100 to 200 feet in diameter.

It may be mentioned here that the water of the large lake of Monte Rotondo, which has a surface area of 18½ acres, has recently been worked for boracic acid. The water of this lake contained originally 1 part in 2000 of boracic acid, but has been concentrated to 2 parts in 1000 by digging a ditch round the lake so as to keep off the rain and surface water.

Of late artificial suffioni have been formed by boring a kind of artesian well and surrounding it with a lagoon. According to Durval, artificial suffioni have been bored to a depth of 160 to 200 feet in the vicinity of Monte Rotondo, and thus yield an annual supply of over 200 tons of boracic acid.

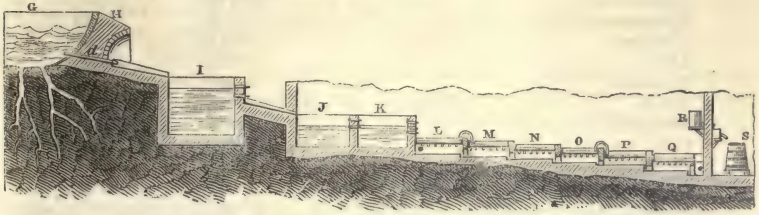


FIG. 120.

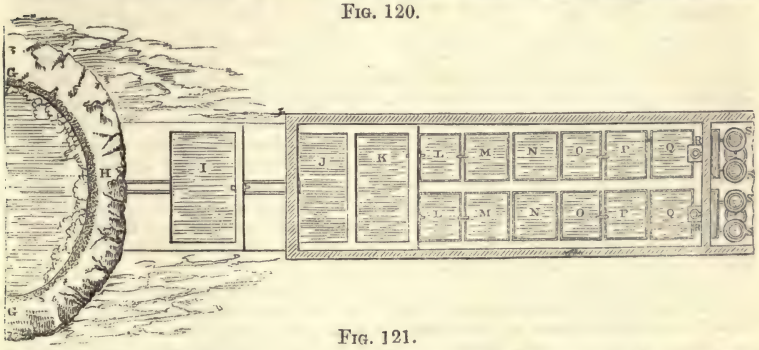


FIG. 121.

A more modern and improved evaporating apparatus is represented in fig. 124. After the solution in the reservoirs (A B) has deposited all the suspended mud, it is decanted into a pan (C) and thence run into a slightly inclined trough made of a sheet of lead 6 feet wide and 130 to 150 feet long, with the edges turned upwards. This trough has an undulatory form; it rests upon wooden sleepers, and is heated by the fumarole vapour. The solution of boracic acid in passing over this heated surface becomes so

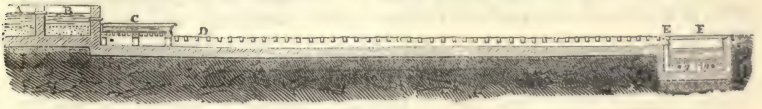


FIG. 124.

concentrated that it is ready for crystallising as it runs off at the other end. It is collected for this purpose in a vessel (F), and treated in the way above described. The fumarole vapour passes first of all under the reservoir (F), thence under the lowest part of the inclined leaden trough, and ascends under the evaporating pan (C).

The preparation of boracic acid from boracite was at one time attempted at Stassfurt, but has been given up. The boracite occurring at Stassfurt is sold direct to the potteries.

Purification.—The boracic acid obtained in the above manner from fumaroles is not pure. The following analysis by Payen shows the varying composition of raw boracic acid :

Crystallised boracic acid	74·00—84·00 per cent.
=41·5—47 anhydrous oxide.	
Hygroscopical water	7·00—5·75
Ammonium sulphate and magnesium sulphate	14·00—8·00
Calcium sulphate, clay, sand, sulphur . .	2·40—1·25
Organic substance, volatile oil . .	2·60—1·00
Ferrous chloride, ammonium chloride	
Hydrochloric acid	
	100·00 100·00

The following table gives the results of two analyses by H. Vohl :

Crystallised boracic acid	80·0912	86·1924
Hygroscopic water	4·5019	1·5240
Sulphuric acid	9·6135	7·8161
Silica	0·8121	0·6861
Sand	0·2991	0·4154
Zinc oxide	0·1266	0·0431
Manganous oxide	0·0031	traces
Alumina	0·5786	0·1736
Lime	0·0109	traces
Magnesia	0·6080	traces
Potash	0·1801	0·4134
Ammonia	2·9891	3·0899
Soda	7·0029	traces
Ammonium chloride	0·1012	0·0321
Organic substance, and loss . . .	0·0918	0·0449

An advantage would be gained by submitting the raw boracic acid to a process of purification on the spot, inasmuch as a marketable product of constant composition would then be obtained, and the removal of the impurities, amounting to about 21 per cent., would lessen the cost of carriage. Payen proposed the following method of purification. The liquor before being admitted into the crystallising vessel is very carefully decanted, in order to remove sand and clay, and the crystals obtained from the clear decanted liquid are submitted to a methodical washing. The wash water is collected, and the boracic acid obtained from it is treated in other purifying operations. The mother liquor might also be distilled with caustic lime, and the ammonia set free collected in sulphuric acid of specific gravity 1·550. Besides this, Payen recommends drying the purified acid at a temperature of 100°, until it has given off one half of its water of crystallisation. Since 100 pounds of acid purified and dried as above correspond to 150 pounds of raw acid, the adoption of this plan on the spot would no doubt well repay the labour involved in carrying it out.

Clouet proposes mixing the crude boracic acid with 4 per cent. of nitric acid, the mixture being allowed to stand a short time, and then heated in a stove. Organic substances are thus destroyed, and ammonia salts volatilised.

Boracic acid is generally purified by recrystallising it, and in some cases solutions of the acid are treated with animal charcoal.

Uses.—The chief use of boracic acid is in the preparation of borax. It is also used for glazing porcelain ; a solution of 1 part of boracic acid in 100 parts of water is used for soaking the wicks of stearine candles. Boracic acid is also used for etching iron and steel, for preparing flint glass, certain chrome greens, pigments, etc. It has been also proposed to use boracic acid for the preparation of nitric acid from Chili saltpetre, so as to obtain borax as a by-product. Boracic acid is also used as a laboratory reagent.

SILICON.

Symbol Si. Atomic Weight 28.

History.—This elementary substance was first isolated by Berzelius in 1823, but its probable existence as a constituent of silica had been suggested by Lavoisier some years previously, and it had actually been obtained in an impure state by Davy and Berzelius.

Occurrence.—Silicon occurs only in the state of combination with oxygen as silica, in a variety of forms, such as quartz, flint, chalcedony, opal, sandstone and sand, also combined with various basic oxides as silicates, constituting a great variety of minerals, rocks, etc. Next to oxygen it is probably the most abundant of all the elementary substances.

Characters.—Silicon is a solid substance capable of assuming three conditions, in the amorphous form it is a dense brownish powder insoluble in water, nitric acid, or hydrochloric acid, but readily dissolved by hydrofluoric acid and solution of caustic alkalies. When heated out of contact with atmospheric air, it melts at a very high temperature, and when heated in the air it burns and is converted into silica. In the graphitic state silicon has the form of hexagonal crystals, and a density of 2·49; it conducts electricity and is not dissolved by acids, but is slowly dissolved by solution of caustic alkali. Silicon also crystallises and assumes the form of hexagonal prisms of a dark steel-grey colour.

Compounds.—Silicon is tetravalent, and in its chemical relations presents considerable analogy to carbon. It combines with hydrogen, fluorine, chlorine, bromine, sulphur, and oxygen, forming compounds represented by the formulæ SiH_4, SiF_4, $SiCl_4$, $SiBr_4$, SiS_2, SiO_2; it also combines with several metals, forming silicides, but these substances are little known, and they do not generally possess any industrial interest. There is but one oxide known, which has a composition represented by the formula SiO_2, and is called silicic oxide or silica; it combines with basic oxides, forming a numerous class of saline substances called silicates, which frequently contain excess of silica, as well as two or more metals or basic oxides, and many of them are double salts. Consequently the composition of the silicates is often very complex, and therefore it is convenient to represent these substances as compounds of silica with basic oxides, rather than by formulæ like those by which many other saline substances are represented. The composition of neutral silicates containing respectively monovalent, divalent, and trivalent metals is represented, according to both methods, by the following formulæ:

$M'_4\ SiO_4$	=	$2M'_2\ O,\ SiO_2$
$M''_2\ SiO_4$	=	$2M''\ O,\ SiO_2$
$M'''_4 3SiO_4$	=	$2M'''_2O_3, 3SiO_2$

A great number of silicates occur naturally in great abundance as minerals, such as felspar, hornblende, augite, etc.: many of the products obtained in smelting operations and known as slag, as well as the various kinds of glass and pottery ware, also consist of silicates, and the characters of hydraulic mortar and cements are due to substances of this nature.

Silicic oxide combines with water, forming several hydrates, none of which, however, have a composition corresponding to the neutral silicates; they are readily decomposed into anhydrous oxide and water, and may be regarded as consisting of neutral hydrogen silicate, H_4SiO_4, or silicic acid combined with excess of silica. The gelatinous precipitate formed on adding hydrochloric acid to a solution of alkaline silicate consists of hydrated silicic oxide, which is insoluble, or only very sparingly soluble in water or in acids. A soluble hydrate is obtained by adding a dilute solution of alkaline silicate to a large excess of hydrochloric acid, and separating the alkaline chloride from the liquid by dialysis; a solution may be thus obtained containing about five per cent. of silica, and by carefully evaporating the water it may be concentrated till the amount of silica in solution becomes as much as 1½ per cent.

The silicates of the alkaline metals are generally soluble in water, but the other silicates are either quite insoluble or only very sparingly soluble in water. Many of the silicates insoluble in water are decomposed by hydrochloric acid or sulphuric acid, and the silica is either dissolved wholly or partially, or it is separated as a gelatinous mass or in a pulverulent state. In any case, however, the silica thus separated becomes insoluble when the liquid containing excess of acid is evaporated to dryness. Some silicates resist the action of all acids but hydrofluoric acid, which decomposes all silicates, converting both the silica and the basic oxides into fluorides.

Most silicates melt when sufficiently heated, and assume a peculiar structure which is termed vitreous, but some silicates require a very high temperature for their fusion. Those silicates are most fusible which contain the most fusible basic oxides and the largest proportion of basic oxide; hence silicates that are but difficultly fusible may be easily melted when mixed with alkalies, or some readily fusible basic oxide, such as litharge, in sufficient proportion to form fusible silicates. The fusibility of a mixture of silicates is generally greater than the mean fusibility of the several silicates in the mixture, and frequently such a mixture melts at a lower temperature than the most fusible of the silicates present would require by itself. On account of this fact it is of great importance that, in metallurgical operations, the addition of the materials used as fluxes in smelting ores should be regulated so as to produce slag of suitable character in regard to fusibility.

Potassium silicates and sodium silicates are very similar in their general characters. They are colourless and, in the vitreous condition, transparent. The compounds K_2O,SiO_2 and Na_2O,SiO_2 are easily fusible, and they are soluble in water, forming an alkaline solution known as *liquor silicum*. The silicates containing four molecules of silica and one molecule of potash or soda, $K_2O,4SiO_2$ and $Na_2O,4SiO_2$, are also soluble in water, and constitute the materials known as water glass. Alkaline silicates containing larger amounts of silica are proportionately less fusible and less soluble in water. As a rule the sodium silicates are more fusible than the corresponding potassium silicates, and in the vitreous condition they have greater brilliancy. The alkaline silicates, when melted in contact with other silicates, readily unite with them in almost any proportions, forming double silicates, the fusibility, colour, and other characters of which vary according to the nature and relative proportions of the basic oxides they contain. The different kinds of glass, enamel, etc., consist of double silicates containing alkaline silicates in considerable amount. The alkaline silicates do not occur naturally, except in combination with other silicates, as double salts, such as felspar, mica, etc.

Calcium silicates are far less fusible than the alkaline silicates; the most fusible compound, represented by the formula CaO,SiO_2, requiring a very high temperature to melt it. This silicate occurs naturally as wollastonite. A disilicate $CaO,2SiO_2,2H_2O$ occurs as okenite, a sesquisilicate as gyrolite, $3(CaO,3SiO_2)8H_2O$. Calcium silicates also occur in combination with potassium silicate as apophyllite, with sodium silicate as pectolite, and with other silicates in a great number of minerals. Many kinds of glass consist of calcium silicates combined with alkaline silicates; thus Bohemian hard glass has a composition approximating to the formula $\begin{cases}3CaO,3SiO_2\\2K_2O,3SiO_2\end{cases}$, and ordinary window glass has a composition approximating to the formula $\begin{cases}CaO,2SiO_2\\Na_2O,2SiO_2\end{cases}$.

The presence of calcium silicate in glass adds to its brilliancy and hardness. The hardening or setting of hydraulic mortar and cements is due to the formation of calcium silicate, and many of the slags obtained in smelting operations contain considerable amounts of calcium silicates. Compounds of calcium silicates, with calcium borates, also occur as datholite, $CaO,2SiO_2.CaO,B_2O_3$, and in the hydrated state as botryolite, $CaO,2SiO_2.CaO,B_2O_3,2H_2O$. A similar compound of calcium silicate with calcium titanate occurs as sphene, $CaO.3SiO_2.2CaO,TiO_2$.

Magnesium silicates are in general respects like the calcium silicates. They occur naturally as minerals, but some portion of the magnesia is generally replaced by other basic oxides. Thus $2MgO,SiO_2$ occurs as forsterite, chrysolite, and olivin; MgO,SiO_2 as augite and hornblende; $3MgO.2SiO_2,2H_2O$ as serpentin. Silica and magnesia combined in various other proportions are also the essential constituents of steatite or talc, meerschaum, chondrodite, etc.

Aluminum silicates are especially characterised by their very difficult fusibility. The neutral silicate, $2Al_2O_3,3SiO_2$, occurs naturally in combination with various proportions of water as certain kinds of kaolin or porcelain clay, and a large number of other compounds of silica with alumina occur either as argillaceous minerals or in the crystallised state as andalusite, cyanite, sillimanite, etc. The different kinds of porcelain, pottery ware, and bricks consist chiefly of aluminum silicates, partially

vitrified by the direct action of heat and by the melting of small proportions of fusible silicates diffused throughout the mass. Aluminum silicates also occur in combination with other silicates constituting the various kinds of felspar, garnet, tourmaline, mica, chlorite, augite, hornblende, zeolites, serpentine, etc. Many of the slags produced in smelting operations consist of double silicates of this kind. Aluminum silicates likewise occur in combination with sulphates as in hauyne, lapis lazuli, etc., with carbonates as in cancrinite, and with fluorides as in lepidolite, topaz, chondrodite, mica, etc.

Ferrous silicates are much more easily fusible than those of calcium or magnesium, especially the compound of silica and ferrous oxide in equal molecular proportions. FeO,SiO_2 also occurs naturally as grünerite and in some augitic minerals. The silicate represented by the formula $2FeO,SiO_2$ occurs naturally as the mineral fayalite, and several of the slags obtained in converting cast iron into malleable iron, as well as in the refining of copper, approximate in composition to this silicate. Ferrous silicates have a dark green colour.

Manganous silicates are analogous in general characters to ferrous silicates. The compound MnO,SiO_2 occurs in some augitic minerals; another silicate having a composition represented by the formula $2MnO,SiO_2$ occurs as tephroite, and together with silicates of iron and zinc in troostite and knebelite.

Lead silicates are very easily fusible; in the vitreous state they are transparent and colourless, or when containing a large amount of lead oxide brilliant, highly refractive, and slightly yellow; these substances are also very soft.

Zinc silicates are analogous to those of lead in general characters. $2ZnO,SiO_2$ occurs naturally as willemite and in the hydrated state as siliceous calamine. Zinc silicate also occurs together with other silicates in troostite and in some augitic minerals.

SILICIC OXIDE (SILICA).

Formula SiO_2. Molecular Weight 60.

History.—The existence of a peculiar earth in rock crystal, flint, and similar minerals was not known until about the middle of the seventeenth century, although the art of making glass and porcelain had long before been carried to a considerable degree of perfection, and even then the true chemical nature of silica was not recognised until Berzelius showed in 1814 that it combines with basic oxides in definite proportions, and that the various minerals containing silica and basic oxides were to be regarded as definite saline compounds.

Occurrence.—Silica occurs crystallised in a pure state as rock crystal and other kinds of quartz; also containing slight admixtures of various metallic oxides, as amethyst, cairngorm, carnelian, chalcedony, and agate. Many sandstones consist almost entirely of coherent quartz granules. Flint consists of silica in a compact state without crystalline structure. In the amorphous state and combined with water, silica occurs as opal and in a variety of other forms. In combination with various basic oxides, silica is a constituent of a very large number of minerals, some of which are comparatively rare, while others are very abundant and constitute the chief mass of entire mountain ranges.

Characters.—In the crystalline state as rock crystal, silica is colourless and transparent; but as it occurs naturally it is often variously coloured, presenting shades of yellow, red, brown, green, or blue, owing to the presence of metallic oxides in small proportions. Sometimes it is quite black. Other kinds of quartz are often opaque, as in the form of flint, and in proportion as the amount of admixtures increases the characters of pure silica are replaced by those of other substances. The density of silica in the crystalline form ranges from 2·5 to 2·8; that of amorphous silica varies from 2·3 to 1·9.

Silica prepared artificially is a white earthy powder; like natural silica, it is perfectly insoluble in water, or in any acid except hydrofluoric acid; both kinds, however, are dissolved gradually when heated with solutions of caustic alkalies, or even solutions of alkaline carbonates. Silica melts only at a very high temperature, forming a transparent vitreous mass; when heated in contact with basic oxides, it combines with them, forming silicates which either melt very readily or form a coherent mass by the softening of the particles. Alkaline carbonates are readily decomposed by silica at a sufficiently high temperature, the silica displacing carbonic dioxide and combining with the alkali to form a silicate.

POTASSIUM.

Symbol K. Atomic Weight 39·1.

History.—Potassium was discovered in 1807 by Sir H. Davy, and the demonstration of its metallic character served to show that potash, or the vegetable alkali, as it was termed to distinguish it from soda or mineral alkali, was in the caustic state the oxide of a metal, and that the salts of potash corresponded in composition with the salts of other metals.

Occurrence.—Potassium does not occur naturally in the metallic state, but only in combination, chiefly with chlorine, bromine, or iodine, or with oxygen and acid oxides, forming salts, which are widely distributed in all three natural kingdoms.

Potassium chloride occurs in large well-formed crystals as the mineral called sylvin, and in the form of a double salt, with magnesium chloride, as carnallite ($KClMgCl_2 + 6H_2O$). Potassium sulphate occurs in alum stone, kainite, schönite, glaserite, etc. Potassium nitrate effloresces from many parts of the earth's surface. Potassium silicate forms one of the essential constituents of a large number of silicates, such as leucite, felspar, mica, glaukonite, phonolithe, etc. Potassium sulphate and potassium chloride are contained in the water of many salt springs, and in sea water, which, when treated for common salt, affords potassium salts as a by-product. Potassium salts are also contained in small quantities in many other kinds of natural water.

Potassium salts occur in plants as phosphates, sulphates, chlorides, and salts of organic acids; the ash remaining when the plants are burnt consists of these salts or carbonates formed by decomposition of the organic acids. Potassium silicate is also a constituent of the ash of most plants. In animals potassium occurs chiefly in the form of phosphates.

Formerly potassium salts were obtained almost entirely by the incineration of plants, and considerable quantities of potash are still derived from this source, as described under the head of 'Potassium Carbonate.'

From the very earliest times sea-weed has been collected on the Scotch and Irish coasts, as well as on the coasts of Normandy and Brittany, either for use as manure or for obtaining the ash by burning it. The process of incineration is carried out at the present day in the following manner:—The sea-weed is either washed on shore by the sea—drift weed—or that growing on the sea coast is cut; it is partly dried in the sun, and then burnt in heaps, piled up over shallow pits until a half-fused ash remains, which constitutes the material called kelp or varec. The composition of the various sorts of kelp differs considerably, as may be seen from the following analyses.

Kelp, which is obtained on the coasts of Scotland and Ireland, as well as on the shores of the Orkney Islands, by incinerating various fuci and other sea-weeds, has, according to Brown, the following percentage composition.

1. *Insoluble Salts.*

Calcium carbonate		2·591
Phosphoric acid		10·556
Basic calcium sulphide		1·093
Calcium silicate		3·824
Magnesium carbonate		6·554
Sand		1·575
Alumina		1·142
Carbon	Unburnt organic substance	0·920
Hydrogen		0·144
Nitrogen		0·152
Oxygen		0·658
		29·209
Water		6·800

2. *Soluble Salts.*

Potassium sulphate	4·527
Sodium sulphate	3·600
Calcium sulphate	0·279
Magnesium sulphate	0·924
Sodium sulphite	0·784
Sodium hyposulphite	0·220
Sodium phosphate	0·540
Sodium carbonate	5·306
Sodium sulphide	1·651
Potassium chloride	26·491
Sodium chloride	19·334
Calcium chloride	0·229
Magnesium iodide	0·316
Magnesium bromide	traces
	64·200

Varec is made on the coasts of Normandy and Brittany by incinerating sea-weed. It has the following composition:

	Villette	Cherbourg	
Potassium sulphate . . .	20·35	22·19	42·54
Potassium chloride . . .	10·53	16·00	19·64
Sodium chloride . . .	54·11	45·78	25·38
Sodium carbonate . . .	13·76	9·53	3·71
Insoluble substance . .	—	1·50	0·73
Iodine compounds . . .	traces	traces	traces
Water	1·25	5·00	8·00

The method of extracting the potassium salts from kelp or varec is described under the head of 'Potassium Chloride.'

One of the most important sources of potassium salts is the enormous salt deposit of Stassfurt and Leopoldshall. The deposit of potassium salts lies upon a very deep layer of rock salt, and is subdivided by Bischof into the following regions:

α. Polyhalite region, which lies immediately above the pure rock salt. This deposit is about 200 feet deep, and consists essentially of impure rock salt, interlaced with veins of polyhalite.

β. Kieserite region, which lies above the polyhalite region. This deposit is about 180 feet deep, and like the above consists essentially of impure rock salt, interstratified with layers of kieserite, sometimes many feet thick.

γ. Carnallite region. This deposit is between 130 and 160 feet deep, and consists of a variable mixture of rock salt and salts of magnesium and potassium. Amongst the latter carnallite prevails, which is the most important salt for the production of potassium chloride. It is chiefly this latter region which contains the salts that are now treated for potassium salts, but were formerly thrown on one side at the period when the only object in view was to get at the deposit of rock salt lying beneath.

The most important minerals of the above three regions are the following:

α. In the polyhalite region.

Polyhalite, which has a composition represented by the formula—

$$2CaSO_4 + MgSO_4 + K_2SO_4 + 2H_2O.$$

β. In the kieserite region.

Kieserite, the composition of which may be represented by the formula—

$$MgSO_4 + H_2O.$$

γ. In the carnallite region.

Carnallite, which has the following composition—

$$KCl + MgCl_2 + 6H_2O.$$

It contains 24 to 27 per cent. potassium chloride, small quantities of sodium chloride and calcium sulphate, as well as traces of ferric oxide, rubidium, cæsium, thallium, and bromine. It is colourless when pure, of a coarse crystalline structure, and deliquescent. The carnallite found among the salts has generally a reddish tinge of more or less depth, owing to the presence of iron mica.

b. Kainite ($MgCl_2 + MgSO_4 + K_2SO_4 + 6H_2O$). Part of the magnesium is always replaced by calcium, and part of the potassium by sodium.

c. Sylvin (KCl). This is probably a secondary product, produced by the magnesium chloride of carnallite having been dissolved out by water.

d. Schönite ($K_2SO_4 + MgSO_4$). This mineral often forms a crust upon the surface of kainite.

Other salts found in the carnallite region are tachydrite (calcium and magnesium chlorides), boracite or stassfurtite (magnesium borate and magnesium chloride), and small quantities of iron mica.

Characters.—Potassium is a solid substance possessing distinct metallic characters; it has a bluish-white colour, with considerable lustre when unoxidised, and its specific gravity is ·865 as compared with water; at ordinary temperatures it is so soft that it can be easily cut with a knife; at 0° it becomes brittle; it melts at about 62°, and volatilises at a red heat. Potassium combines very readily with oxygen, and on that account requires to be kept immersed in a liquid hydrocarbon, such as naphtha; it absorbs oxygen from atmospheric air at the ordinary temperature; when heated in

contact with air, it takes fire, and burns with a violet-coloured flame; it decomposes water, and displaces half its hydrogen, forming potassium hydrate, $H_2O + K = KHO + H$, and the hydrate dissolves in the water, forming a solution of caustic potash.

Preparation.—Potassium is prepared by heating to a very high temperature a mixture of potassium carbonate and charcoal, obtained by heating to redness acid potassium tartrate, in a covered crucible, until it ceases to give off vapour. The black porous residue is rapidly cooled, broken into small lumps, and put into a wrought-iron mercury bottle (*b*), which is supported in a furnace as shown by fig. 125, and fitted with a short iron tube (*d*), which serves to conduct the potassium vapour into a condenser (*c*), the construction of which is shown on a larger scale by fig. 126. This condenser consists of two pieces of sheet iron, *a* and *b*, fitted together with clamps so as to form a shallow box about a quarter of an inch deep; it is open at both ends, and the narrow end fits upon the iron tube of the mercury bottle. Upon heating the mercury

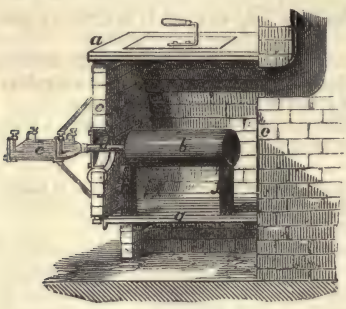


Fig. 125.

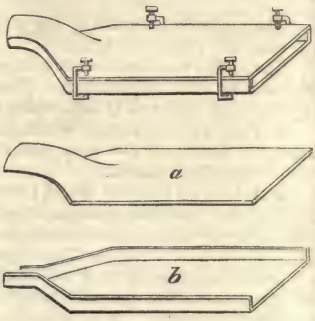


Fig. 126.

bottle to a reddish-white heat, the potassium carbonate is decomposed by the charcoal, and the potassium thus reduced escapes in vapour together with carbonic oxide gas, and is condensed in the narrow sheet-iron box, which is kept cool by wet cloths.

Compounds.—Potassium combines with oxygen in three proportions, forming a monoxide K_2O, which is a powerful basic oxide and combines with acid oxides forming salts; a dioxide, K_2O_2, which is analogous in its characters to hydric peroxide, and a tetroxide, K_2O_4. The compounds of potassium with fluorine, chlorine, bromine, iodine, sulphur, are saline substances that will be described separately.

POTASSIUM OXIDE.

Formula K_2O. Molecular Weight 94·2.

This substance is formed when potassium, in thin slices, is exposed to air free from moisture and carbonic dioxide, or by heating potassium hydrate with potassium; it is a white solid substance, very deliquescent and caustic; it melts at a red heat and volatilises at a higher temperature.

POTASSIUM HYDRATE.

Formula KHO. Molecular Weight 56·1.

The substance commonly called caustic potash may be obtained by dissolving potassium oxide in water, or more conveniently by decomposing potassium carbonate dissolved in water by means of caustic lime, which abstracts the carbonic dioxide, and forms calcium carbonate, leaving potassium hydrate in solution, according to the equation:

$$K_2CO_3 + CaH_2O_2 = CaCO_3 + 2KHO.$$

The operation is conducted in the same manner as the preparation of sodium hydrate (*vide* that article).

Characters.—Potassium hydrate is a white solid substance having a specific gravity of 2·1. It melts below a red heat to an oily liquid and volatilises at a higher temperature. It rapidly absorbs moisture from the atmosphere and deliquesces; it

also absorbs carbonic dioxide, and forms potassium carbonate. It dissolves in about half its weight of water, evolving great heat, and is extremely caustic both in the solid state and in solution.

POTASSIUM CHLORIDE.

FORMULA KCl. MOLECULAR WEIGHT 74·6.

Occurrence.—Potassium chloride occurs naturally in a pure state as sylvin round the fumaroles of Vesuvius, and in the salt deposits of Stassfurt and at Kalucz in Hungary. It also occurs very abundantly in combination with magnesium chloride as carnallite in the salt deposits of Stassfurt, which are extensively worked. Potassium chloride also occurs in sea water, in kelp, or the ash of sea-weeds, in natural brines, and in the water of some mineral springs.

Michels represents the salts excavated from the Stassfurt mine and delivered to the potash works as having the following percentage composition:

Carnallite	50–55 per cent.
Rock salt	25–30 „
Kieserite and kainite	10–15 „
Anhydrite, clay, sand, etc.	15–0 „

This amount of carnallite represents from 13 to 14 per cent. of potassium chloride. The salt obtained from the Leopoldshall mine contains on the average a larger amount of carnallite than that from the Stassfurt mine, the amount of potassium chloride ranging from 15 to 17 per cent.

Characters.—Potassium chloride is readily soluble in water; it crystallises in cubes, and presents many resemblances to sodium chloride or common salt. It has, however, a stronger taste, and cannot be taken into the system in such large quantities as common salt without injury. Crystals of potassium chloride decrepitate when heated, the salt then melts, and at a sufficiently high temperature it volatilises; it is much more easily volatilised than sodium chloride.

The potassium chloride of commerce is generally impure, and contains only from 80 to 90 per cent. of pure chloride, the remainder consisting chiefly of sodium chloride, sulphates in variable amount, some insoluble substance, and water. When potassium chloride has been prepared from molasses residue, it is generally mixed with alkaline carbonates.

Frank gives the composition of a good sample of potassium chloride as follows, and the other analyses are by Tissandier.

	Frank	Tissandier		
Potassium chloride	86·14	79·80	93·52	75·01
„ sulphate	—	12·31	4·01	11·81
„ carbonate	—	1·00	0·61	3·28
Sodium carbonate	—	2·10	—	2·13
„ chloride	10·94	—	—	—
Magnesium sulphate	0·24	—	—	—
Insoluble matter	0·45	0·32	0·28	0·90
Water	4·29	4·27	1·38	6·35

Preparation.—The greater part of the potassium chloride of commerce is now made from carnallite; but considerable quantities are obtained as by-products of various industrial operations, as in the preparation of salt from sea water, and the preparation of iodine from kelp; potassium chloride is also obtained from the residues of beet sugar molasses. The preparation of potassium chloride from the sylvin found at Kalucz in Hungary, which is mixed with a great quantity of clay, has not at present obtained any great dimensions, although it will probably soon do so. Small quantities of pure potassium chloride are even now prepared from potashes.

WORKING OF STASSFURT SALTS.—The methods of preparing potassium chloride adopted in the works of Stassfurt and Leopoldshall are different. They are alike in this respect, that carnallite is lixiviated, either with water or a lye poor in magnesium chloride, the lixiviating liquor being employed hot. The magnesium chloride and the potassium chloride of the carnallite dissolve, but upon cooling the liquor, potassium chloride alone crystallises out, since carnallite only crystallises from a liquor containing a large excess of magnesium chloride. However, upon evaporating the mother liquor

from the first crystallisation to a certain density, artificial carnallite crystallises out, owing to the liquor having become proportionally richer in magnesium chloride by the former crystallisation of potassium chloride. The artificial carnallite is separated from the mother liquor and once more dissolved and the liquor crystallised, whereupon a further crop of crystals of potassium chloride is obtained.

A method much in use at Stassfurt and Leopoldshall is the following:

Breaking up of the Salts.—The carnallite as it comes from the mine is either crushed to a coarse powder in a mill, or it is simply broken up with hammers into pieces about the size of one's hand.

In order to reduce the salts to a powder, Frank has recently introduced an apparatus which he calls a disintegrator; but it appears that the mills formerly employed do better work.

Solution of the Salts.—The broken or powdered salt is lifted by a mechanical arrangement into a higher story, where the dissolving operation is carried out.

The lixiviating vessels are made of iron plates riveted together. They are cylindrical in shape, and have a diameter of between 6 and 10 feet, and a depth of from 8 to 10 feet, being capable of holding 100–300 cwts. of carnallite, together with the water required for the solution of the same. The vessels are furnished with perforated false bottoms about six inches from the bottom, for supporting the carnallite during the process of lixiviation. The bottom of the pan slopes towards the centre, so as to admit of the liquor being run off with facility through a tap at that point. A rod by which the tap can be closed or opened, as desired, projects above the lixiviating pan. Over the tap is a perforated iron cylinder, which extends above the surface of the liquid for the purpose of holding back fragments of the undissolved salt. There is also a manhole above the perforated false bottom, for removing the undissolved residue. Heat is applied by blowing steam into the pan, through a pipe running round the pan between the bottom and perforated shelf. Beneath the lixiviating pan are placed several tanks of sheet iron, in which the liquors are allowed to settle; and to prevent them from cooling too rapidly, they are surrounded by brickwork, or some other non-conducting material.

When the carnallite is added to the liquor in the lixiviating pan, the temperature must be kept up to the boiling point, the addition being continued until the turbid solution has a specific gravity of 1·282, or the clear solution a specific gravity of 1·277. The liquor is then run off into the settling tanks below. The operation should be conducted as rapidly as possible, in order to reduce to a minimum the solution of potassium sulphate, which dissolves more slowly than the chloride. After the solution has been run off, large masses of undissolved salts remain, containing a considerable quantity of potassium chloride; and on this account the residue is treated a second time with water or weak liquor from a previous operation, the whole heated by blowing in steam, and the solution, run off into settling tanks, is afterwards used in place of water for operating upon fresh carnallite.

The residue left after the second treatment of the salt with water amounts to about 25 per cent. and consists of kieserite, rock salt, anhydrite, etc., with about 5 per cent. potassium chloride. It is either thrown aside as waste or worked up for magnesium sulphate.

To obtain the potassium chloride, the clear liquor is run while hot from the settling tanks into crystallising pans made of sheet iron, about 2 feet deep. After the lapse of 24 or 48 hours, the mother liquor is drawn off, and the salt deposited upon the sides of the pans is removed to vessels fitted with perforated false bottoms, in which it is washed with water so as to remove all adherent mother liquor. This operation is repeated several times, according to the degree of purity the salt is required to have, and the residue, containing from 80 to 90 per cent. of potassium chloride, is finally dried and sifted.

The mother liquor from the crystallising pans is evaporated until it has a specific gravity of 1·299, when it deposits sodium chloride and some potassium sulphate, which is used either for manure or for salting cattle food. The clear liquor drawn off from this salt contains a large amount of magnesium chloride, together with some potassium chloride, and by concentration it deposits these salts as artificial carnallite, which is worked as already described for the separation of potassium chloride.

The last mother liquor from the crystallisation of carnallite is sometimes used for the first solution of the crude carnallite salt, by which means the impurities are separated and the double potassium and magnesium chloride is obtained in such a state that, on treatment with water, it yields at once very pure potassium chloride. In other works the last mother liquor is either evaporated down to obtain magnesium chloride, or worked for the extraction of the bromine it contains (see p. 178).

Extraction from the Ash of Sea-Weed.—The amount of potassium chloride in

some kinds of sea-weed is sufficiently large to make the extraction of this salt desirable, and it is carried out in connection with the manufacture of iodine.

Lixiviation of the Kelp or Varec.—This operation is performed in the same way as lixiviation of ball soda (*vide* this article). The fused semi-vitreous mass is first broken into small pieces, and then lixiviated with water. The apparatus used for this purpose varies considerably in form. In some places square iron vats with double bottoms are used, the upper or false bottom being perforated. Upon this perforated bottom the broken kelp is placed, and water is added in quantity sufficient to cover the kelp. After a lapse of a few hours, the liquor is drawn off by means of a cock fitted between the two bottoms, and let into a second vat of like construction filled with kelp; the partly lixiviated mass in the first vat being treated again, either with water or with dilute liquor. About six lixiviating vats of this description are placed in connection with one another, the process being so conducted that fresh water flows first into that vat which contains the most exhausted material, and from thence successively into those vats containing less exhausted material. When the kelp in the first vat is completely exhausted, it is taken out and a fresh charge put in, and fresh water is run into the second vat, and so on to the last vat; and finally into the first, because that will then contain the least exhausted material. This method of lixiviation secures the greatest possible exhaustion of the kelp, with the least possible quantity of water.

The lixiviation is sometimes carried out in the apparatus shown in fig. 127, which consists of five iron vats (A to E), arranged at different levels. In each vat there

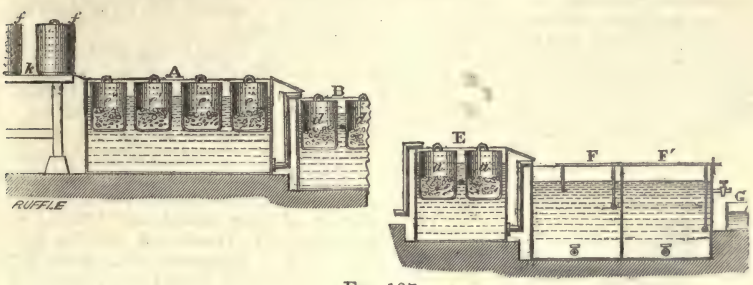


FIG. 127.

are perforated boxes (*a* to *e*) containing pieces of kelp, and supported by iron rods. The highest vat (A) is twice as large as any of the others, and it has two pairs of perforated boxes (*e e e e*). Water let in from above extracts the soluble constituents in the first series of boxes (*e e e e*), and when the liquid has reached the level of the discharge pipe (*d*), it flows out from the bottom of the vat into the upper part of the second vat (B), from thence in like manner into the third, fourth, and fifth vats successively. The liquid discharged from the last vat (E) into the reservoir (F) will have a specific gravity of 1·18 –1·25. When the material in the first series of perforated boxes is sufficiently exhausted, the boxes are hoisted out from the vat and placed to drain upon the support (*k*). The boxes in the second vat (B) are then transferred to the vat (A), those of the third vat to the second vat (B), etc., fresh pieces of kelp being placed in the fifth vat (E). In this way also fresh water comes first of all into contact with the most exhausted material, and thus effects as complete an exhaustion as possible. At the works of Cournerie, in Cherbourg, the liquor is heated by steam, in vats furnished with double sides.

The liquor is allowed to settle in the reservoirs (F F'), and then drawn off into a series of iron pans (G), placed near the reservoirs, where it is evaporated. These pans are arranged in steps one above the other, so that the liquor of the first pan (G) flows into the second pan and from thence into the pan (I, fig. 128), etc., until it arrives at the last pan (K). The pans are heated by a single furnace (*i*), placed under the lowest pan (K), and the hot air is passed along under the other pans. The pan (G), which is furthest away from the furnace, is consequently not heated so much as the

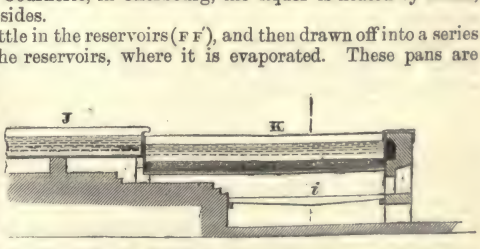


FIG. 128.

others; and the temperature of each pan increases with its proximity to the furnace. In proportion as the liquor is heated, the water evaporates; and a portion of the less soluble salts, such as potassium sulphate and common salt, is often deposited in the pan (1). In order to prevent the deposited salt from adhering to the hot part of the pan immediately in contact with the fire, the bottom of this pan has the shape shown in section by fig. 129. The precipitated salt collects at the sides (*l l*), where the heat is not so great, and it is taken out by means of a perforated ladle. After a short time the liquor is drawn off into crystallising pans, where it deposits, upon cooling, chiefly potassium chloride, together with small quantities of sodium and potassium sulphates. The mother liquor is once more concentrated in specially adapted pans, the salts which separate out meanwhile, such as sodium chloride and sulphate, etc., are removed with a perforated ladle, and the liquor again set to crystallise. Potassium chloride then crystallises out; the liquor drawn off, again evaporated, and allowed to crystallise, generally yields another crop of crystals of impure potassium chloride.

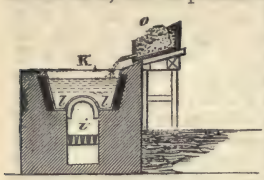


FIG. 129.

The residues remaining in the perforated boxes are further lixiviated with water, and the liquor obtained is evaporated in pans like the first. Sodium sulphate separates in the evaporating pans, and the further operation of crystallising yields potassium chloride. A repetition of these operations yields common salt in the evaporating pans, and impure potassium chloride in the crystallising pans.

The last liquor obtained from the residues, having a specific gravity of between 1·000 and 1·070, is used instead of water for a fresh operation.

The salts separated out either in the evaporating or crystallising pans such as potassium chloride, common salt, potassium sulphate, Glauber's salt, and soda, are separately collected, and, after being washed or recrystallised, are sent into the market.

Payen suggests the evaporation of the concentrated lye in a pan (B B′), having a form like that shown in fig. 130, heated by a fire (A). Directly the precipitation of salts sets in, a sieve (C), supported by a chain moving upon rollers (*d′d″*), and admitting of being raised and lowered by the weight (*e*), is lowered into the pan. The sieve is furnished with three feet which support it inside the evaporating pan, and keep it at a distance of six inches from the bottom. The salts as they precipitate are forced to the surface by the boiling liquid, and in falling back are caught in the sieve. As soon as the sieve is full it is drawn up, allowed to drain for a short time, and its contents emptied on to a shelf; so that the mother liquor adhering to the crystals may drain off into the evaporating pan.

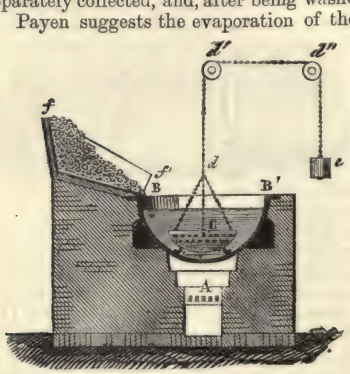


FIG. 130.

Treatment of the mother liquor.—The mother liquor obtained by the operation above described still contains minute quantities of all the salts contained in the original liquor, such as sodium chloride, potassium sulphate, sodium sulphate, and carbonate and potassium nitrate, together with iodides, bromides, cyanides, sulphides, and bisulphites of sodium and potassium, and small quantities of unburnt organic substance.

Uses.—Large quantities of potassium chloride are used for converting sodium nitrate into potassium nitrate, also as manure, and in the manufacture of potassium sulphate and other potassium salts.

POTASSIUM BROMIDE

FORMULA KBr. MOLECULAR WEIGHT 119·1.

This salt is prepared either by dissolving bromine in solution of caustic potash, evaporating to dryness, and heating the residue mixed with charcoal until it is red hot, or better still, by treating iron immersed in water with bromine, and precipitating the solution of ferrous bromide thus formed with potassium carbonate.

Potassium bromide may also be obtained by passing sulphuretted hydrogen into water containing a layer of bromine, saturating the hydrobromic acid thus produced with barium carbonate (witherite), and decomposing the solution of barium bromide with potassium carbonate.

According to Frank's method, bromine vapour, containing chlorine as it escapes from the Woulfe's bottle (D, fig. 106), is conducted through a leaden tube into a second Woulfe's bottle, filled with moist iron filings, and from thence into an open pot also containing iron filings. A mixture of iron chloride and bromide is formed in the Woulfe's bottle at first, but towards the end of the operation, when the evolution of chlorine gradually increases, the bromine is displaced by it from the bromide formed in the Woulfe's bottle, and passing into the open pot, it forms pure ferrous bromide, the whole of the chlorine remaining in the Woulfe's bottle. The ferrous bromide is then decomposed with potassium carbonate. The iron and water may be replaced by a solution of caustic potash, in which case there is first of all formed potassium chloride and bromide, as well as potassium bromate and chlorate; the bromine is, however, eventually displaced by the excess of chlorine, and pure bromine distils over into the caustic potash solution in the second vessel. The liquor thus obtained is then mixed with charcoal, evaporated, and ignited to convert the bromate into potassium bromide.

If opaque crystals of potassium bromide are required, the solution from which the salt is crystallised must be slightly alkaline. Since the mother liquor obtained in this way is very alkaline, it is neutralised as nearly as possible with hydrobromic acid, and again evaporated for a new crop of crystals.

Transparent crystals of potassium bromide are always formed from perfectly neutral solutions, also when the solution contains traces of lead or tin, etc.

Artificial Sea Salt.—This consists of common salt containing varying proportions of bromine in the form of magnesium bromide, which is prepared by precipitating a solution of ferrous bromide with caustic lime, decomposing the calcium bromide with magnesium sulphate, separating the precipitated gypsum, and evaporating the solution to dryness. The consumption of artificial bathing salt from Frank's manufactory alone amounted in 1871 to about 50 tons.

POTASSIUM IODIDE.

Formula KI. Molecular Weight 166·1.

Characters.—Potassium iodide crystallises in cubes; it is soluble in water and in alcohol, and may be prepared by the direct combination of potassium and iodine. For its preparation, however, other methods are used.

Preparation.—The most usual way of preparing potassium iodide is by acting upon a solution of caustic potash with iodine. Iodine is added as long as it is dissolved without colouring the liquid, potassium iodide and iodate being formed, as shown by the following equation:

$$6I + 6KHO = 5KI + KIO_3 + 3H_2O.$$

The solution thus obtained is mixed with a small quantity of powdered charcoal, and evaporated to dryness. The residue is slightly ignited, so as to secure the reduction of potassium iodate, which takes place, as shown by the following equation:

$$KIO_3 + 3C = KI + 3CO.$$

The residue contains accordingly the entire quantity of iodine in the form of potassium iodide. It is lixiviated with water, and the solution evaporated until it has a specific gravity of 1·867, and set aside to crystallise. The crystals are thrown upon funnels, so as to drain off the mother liquor, and then dried by spreading them out upon glazed iron plates, in a current of air of a temperature of 120°–125°.

Instead of heating to redness with charcoal, the reduction of the iodic acid may be effected in the wet way by treating the solution containing iodate with reducing substances, such as hydrated ferrous oxide, sulphurous acid, etc.

Potassium iodide may also be prepared by treating iron with iodine, in presence of water, so as to form solution of ferrous iodide, which is then precipitated with potassium carbonate, the liquid filtered and evaporated to crystallisation.

Liebig's method is to digest amorphous phosphorus with iodine, under water, so as to form in the first instance phosphorus pentiodide, which is immediately decomposed into hydrogen iodide and phosphoric acid. The liquid thus obtained is saturated with baryta water, to remove the phosphoric acid, which is precipitated as barium phosphate, while the iodine remains in solution as barium iodide. The solu-

tion is filtered off, treated with potassium carbonate or sulphate, to precipitate the barium as carbonate or sulphate, which is separated by another filtration, and the clear liquid containing potassium iodide in solution is evaporated to crystallisation.

Wagner recommends adding iodine to a mixture of milk of lime and calcium sulphite with water, so as to form calcium iodide, and then to decompose the solution of that salt with potassium carbonate, separate calcium carbonate by filtration, and evaporate the filtrate containing potassium iodide to crystallisation.

POTASSIUM CHLORATE.

FORMULA $KClO_3$. MOLECULAR WEIGHT 122·6.

History.—This salt appears to have been known in the early part of the seventeenth century to Glauber, who described a kind of saltpetre prepared by means of common salt. Higgins, in 1786, also pointed out that a kind of saltpetre was produced by the action of chlorine upon alkalies, and about the same time it was investigated by Berthollet, but the true composition of this salt was first determined by Gay-Lussac in 1814.

Characters.—Potassium chlorate is an anhydrous salt. It is sparingly soluble in cold water, more readily soluble in hot water. The degree of solubility of potassium chlorate in 100 parts of water at various temperatures is shown in the following table:

At 0° . .	3·33 pts.	At 35·02° . .	12·05 pts.
„ 13·32° . .	5·60 „	„ 49·08° . .	18·96 „
„ 15·32° . .	6·03 „	„ 74·89° . .	35·40 „
„ 24·43° . .	8·44 „	„ 104·78° . .	60·24 „

Potassium chlorate crystallises out from its aqueous solution in laminæ of a pearly lustre; it has a cooling taste resembling nitre. When gently heated, potassium chlorate melts without decomposition; a stronger heat converts it first into potassium chloride (KCl) and perchlorate ($KClO_4$), and at a still higher temperature the whole of the oxygen is given off, potassium chloride remaining:

$$KClO_3 = KCl + 3O.$$

According to the above equation, therefore, potassium chlorate, when subjected to a very strong heat, yields 39·16 per cent. of free oxygen, and 60·84 per cent. of potassium chloride.

One of the most important properties of potassium chlorate is its extremely energetic oxidising action: when mixed with combustible substances, such as sulphur charcoal, or phosphorous acid, explosions of a most violent nature may occur if the mixture is slightly warmed or rubbed. On this account, it is necessary to be very cautious in working with potassium chlorate, and on no account should it be triturated or heated with easily combustible bodies.

Preparation.—Potassium chlorate may be prepared by passing chlorine into a concentrated solution of caustic potash or potassium carbonate. The following equation shows the reaction which takes place:

$$3K_2CO_3 + 6Cl = 5KCl + KClO_3 + 3CO_2.$$

The apparatus used for this purpose consists of a chlorine generator (fig. 103, page 164), and the absorption vessels containing the solution of potash are arranged in a manner similar to that shown and described for the absorption of sulphurous acid (fig. 46, page 106). Between the absorption vessels and the generators is a washing arrangement. At the beginning of the operation there is formed in the first carboy, potassium hypochlorite and chloride, as well as acid carbonate, and if the generation of chlorine is stopped at this point, and the carboy allowed to cool slightly, the greater part of the potassium chloride crystallises out, and may be separated by decanting off the solution. When chlorine is again passed into the decanted liquid, potassium chlorate is formed. The liquid soon becomes saturated with the salt, which separates out in a crystalline condition. Potassium chlorate thus prepared is washed with a small quantity of cold water, to get rid of potassium chloride, and is then crystallised from hot water. According to this method, as may be seen from the above equation, only about one sixth of the potash used is converted into chlorate; the remaining five-sixths, though not absolutely lost, are converted into potassium chloride, which is a far less valuable substance.

In order to convert the entire quantity of potash into potassium chlorate, part of the potash is replaced by lime. The following reaction then takes place:

$$2KHO + 5CaH_2O_2 + 12Cl = 5CaCl_2 + 2KClO_3 + 6H_2O.$$

In this case the entire quantity of potash used is converted into potassium chlorate, the mother liquor yielding calcium chloride instead of the corresponding salt of potassium.

Instead of passing chlorine into a mixture of caustic potash and lime, it is sometimes convenient to pass the chlorine direct into milk of lime, and afterwards to decompose the calcium chlorate with potassium chloride. The apparatus used for the preparation of calcium chlorate consists of a chlorine generator and washing and absorption vessels, the latter being lined with lead and furnished with stirrers, so as to bring the lime into intimate contact with the chlorine. The milk of lime is prepared by mixing lime with five parts water. Chlorine gas is passed into this as long as it is absorbed. The temperature of the liquid rises very quickly upon the introduction of chlorine to 95°; at which temperature the formation of calcium chloride and chlorate takes place. The saturated lye is run from the absorption vessels into tall vessels, where it is allowed to clarify. From the clarifiers the liquid is drawn off by means of siphons into evaporating pans, where it is evaporated, and when it has attained a spec. grav. of 1·180, it is mixed with potassium chloride. It is then further evaporated till a spec. grav. of 1·280 has been reached, and at this point it is allowed to cool. The crystals that form are separated and the mother liquor again evaporated to obtain another crop of crystals. Sometimes a third crystallisation is attempted. The crystals from the first crystallisation are recrystallised once from hot water, those of the second crop generally twice, in order to get rid of the admixture of calcium chloride. The mother liquors are evaporated to obtain the calcium chloride.

Properly prepared potassium chlorate ought not to decrepitate when heated; *i.e.* it ought not to contain any mother liquor mechanically enclosed. Dilute solutions of the salt should give no reaction either with a solution of silver nitrate (chlorine) or with a solution of barium nitrate (sulphuric acid). When strongly heated it ought to decompose with quiet effervescence and the residue should not exceed 60 or 70 per cent. Should the residue exceed this amount, the potassium chlorate is contaminated either with potassium chloride or some other salt. 3·78 grammes of potassium chlorate ought to yield 1 litre of oxygen gas at 0° and under a pressure of 760° mm. of mercury.

Uses.—Attempts have been made to use potassium chlorate in the preparation of gunpowder, but they did not succeed, the powder thus prepared having two disadvantages. (1.) It exploded upon the slightest friction and (2) its decomposition was so sudden and violent that often the guns in which it was employed burst. It was supposed that this difficulty might be got rid of by the addition of nitre, but the explosion was still too violent.

Potassium chlorate is used in preparing percussion caps, fusees for cannon, etc. The following gives the composition of two mixtures of the kind.

Potassium chlorate	27·5	26
Fulminating mercury	12·3	13
Nitre	30·7	30
Sulphur	16·3	17
Powdered glass	11·2	14
Glue or gum	1·0	1

The charge for a copper percussion cap weighing 78 milligr. is 25 milligr. of the above mixture, so that 1 kilo of the mixture serves for 40,000 such caps. The caps for fowling-pieces contain only 15·20 milligr. of the explosive mixture. The mixture is put into the caps in a moist state and left to dry in them.

Potassium chlorate is much used in pyrotechnics, and it has found extensive employment in the manufacture of the patent safety matches, which are free from phosphorus.

At one time considerable quantities of potassium chlorate were used in the preparation of the so-called chemical matches, which were ignited by dipping them in concentrated sulphuric acid. The ignitable part of these matches consisted of a mixture of equal parts of potassium chlorate and sulphur together with a small quantity of lycopodium, or resin, and cinnabar. The ends of the wood splinters for making the matches were first of all dipped in sulphur, and then the above mixture was made to adhere to the sulphur by means of gum. Upon pressing the head of such a match against asbestos saturated with sulphuric acid, the match ignited and the sulphur enabled it to communicate the fire to the wooden portion of the match. These matches have been, however, entirely replaced by phosphorus lucifer matches (*vide* Phosphorus).

Matches without Phosphorus.—There are many recipes for preparing combustible compositions without phosphorus in either of its forms. The following are given by Canouil, and are said to ignite when rubbed against sand or glass paper:

I.		II.	
Potassium chlorate	5	Potassium chlorate	6
Crocus of antimony	0·5	Sulphur	0·5
Oxidised red lead	3	Lead cyanide	2
Gum	2	Gum	2
Water	8	Water	8

III.		IV.	
Potassium chlorate	5	Potassium chlorate	28·5
Glass	3	Glue	5·4
Potass. bichrom.	2	Potass. bichrom.	2·9
Gum	2	Lead nitrate	2·7
Water	8	Powdered glass	10·8
		Sulphur	85·0

Canouil gives further a recipe for preparing matches to be struck on a specially prepared surface, both match and friction surface being free from phosphorus.

Combustible Composition.		*Friction Surface.*	
Potassium chlorate	7·3	Potassium chlorate	6
Lead nitrate.	2·3	Iron scales.	1
Acid potass. chromate.	2·3	Red lead	1
Sulphur	1·3	Glue (in quantity sufficient to cause the mass to adhere)	
Gum	6·3		
Water	18·0		

Wagner considers Wiederhold's composition the best. It has the following composition:

Potassium chlorate	7·8
Lead hyposulphite	2·6
Gum arabic	1·0

The combustible composition ordered by the French Academy for making matches used in barracks consists of—

Potassium chlorate	90 parts
Acid potassium chromate	45 „
Lead peroxide	25 „
Red lead	20 „
Crocus of antimony	20 „
Antimonous sulphide	15 „
Glass	15 „
Potassium ferrocyanide	5 „
Gum	15 „
Water	55 „

The composition requires somewhat strong friction for ignition, but lessens on that account the danger of accidental ignition.

Jettel gives the following theoretical principles upon which the action of the non-phosphorus matches depends:—1. The chief active constituent is potassium chlorate, the quantity of which varies between 40 and 92 per cent., but being generally over 60 per cent. 2. Most of these compositions contain from 10 to 40 per cent. of other oxidising substances. 3. When sulphur is used, a quantity is taken equal to 25 per cent. of the potassium chlorate employed. When metallic sulphides are used instead of sulphur, a relatively greater quantity of them is required. 4. Powdered glass, sand, water, etc. are added to moderate the force of the explosion. 5. The quantity of thickening material employed is equal to about $\frac{1}{3}$–$\frac{1}{2}$ of the amount of oxidising salts. If the former be in too great excess, ignition is rendered difficult.

A not unimportant use of potassium chlorate is in calico-printing for producing certain tints. For this purpose the dye is mixed with the required amount of potassium chlorate, and laid on the stuff, which latter is then exposed to a steam pressure of 3 or 4 atmospheres, so as to fix the colour. The potassium chlorate undergoes decomposition in contact with the organic substances, and exercises an oxidising action upon the colouring matter, so producing the desired changes.

Potassium chlorate is further very considerably used in chemical laboratories, in

the preparation of oxygen gas, for the oxidation of organic substances in toxicological researches, and for oxidising metals, etc.

POTASSIUM CARBONATE (POTASH).

Formula K_2CO_3. Molecular Weight 138·2.

History.—This substance was known and used in the earliest times in the form of the ashes obtained by burning plants, and commonly called potash. The first account of the preparation of potassium carbonate in a purer state is found in the writings of Aristotle, who describes a salt, obtained in Umbria from the ashes of reeds and rushes, which, from the properties ascribed to it, can have been nothing else than potassium carbonate. Dioscorides also describes the alkaline properties of the liquor obtained by lixiviating the ashes of plants with water, but he does not mention the solid residue obtainable by evaporating the liquor. The same author however describes the preparation and properties of potassium carbonate, obtained by heating tartar to redness, but without indicating that it is identical with the substance contained in the liquor obtained by lixiviating the ash of plants. The Romans used potassium carbonate chiefly for medicinal purposes, and in preparing soap. At a later period the Arabian chemist Geber, and also Albertus Magnus, Raymond Lully, Glauber, and others, gave directions for preparing potash. Kunkel ascertained that the salt obtained by lixiviating the ash of plants is identical with the salt obtained by exposing tartar to a red heat; before his time it was generally supposed that the different materials yielded different alkalies.

Characters.—Potassium carbonate is a colourless salt, very soluble in water; it deliquesces upon exposure to the air, for which reason it requires to be kept in well-closed vessels. It melts at a red heat. Potassium carbonate crystallises from its aqueous solutions with 2 molecules of water.

Crude potash is generally contaminated with foreign ingredients, which vary in nature and amount according to the materials from which it has been obtained, as may be seen from the following table:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Potassium carbonate.	74·10	62.6	68·07	41·7	71·38	69·61	53·90	32·9	44·28
,, hydrate .	—	—	—	49·6	—	—	—	—	—
Sodium carbonate .	3·00	11·0	5·85	1·4	2·31	3·09	23·17	18·5	13·48
Potassium sulphate .	13·47	15·5	15·32	4·0	14·38	14·11	2.98	14·0	5·71
,, chloride .	0·95	4.0	8·15	2·0	3·64	2·09	19·69	16·0	18·86
Water . . .	7·28	6·9	—	1·3	4·56	8·82	—	18·6	4·00
Insoluble matters .	1·20		2·64		2·73	2·28	0·26		13·50

I. and II. are potash, from Tuscany, analysed by Pesier. III. rock ash, from America, analysed by Pesier. IV. pearl ash, analysed by F. Mayer. V. Russian potash, by Pesier. VII. French potash, from molasses mud, analysed by Pesier. VIII. potash from Magdeburg, analysed by Grüneberg. IX. French potash (from department de l'Aisne), by Tissandier.

The following are the chief varieties of potash met with in commerce:—

1. *German Potash* (Stassfurt).—1st quality, white, dry, and friable, dissolving almost entirely in 4 parts of water, and containing about 90 per cent. of pure potassium carbonate, with, at the most, 3 per cent. of soda.

2. The same, partially purified, almost colourless, crumbly, and friable, containing at least 80 per cent. of potassium carbonate, and up to 6 per cent. of soda.

3. *Illyrian Potash.*—White, dry, granular, containing at least 80 per cent. pure potash and from 2–3 per cent. of soda.

4. *American Potash.*—*a.* Pearlash, very fine quality. *b.* Rock ash, owing to its high price less often met with than Nos. 1 and 2; contains about 74 per cent. pure potash, and almost always considerable quantities of caustic potash.

5. *German and Moravian Beet Potash.*—Greyish white hard granules, leaving a considerable residue when treated with 4 parts water; contains from 70 to 75 per cent. of alkaline carbonate and caustic alkalies, of which from 12 to 18 per cent. is soda.

6. *Russian Potash* and Kasan ash.—True wood ash. *a.* Granular powder of an unequal degree of hardness; colour, partly greyish-white, partly dirty, sometimes green, from the presence of potassium manganate, or reddish, from the presence of iron oxide; yields a considerable residue, even when treated with a large quantity of water. Total

quantity of alkalies about 60 per cent. *b.* Sunflower ash, consists of granules and powder of a greyish-white colour, more uniform than the previous sort; leaves a considerable residue when treated with water, and contains about 50 per cent. of alkalies.

Preparation.—Potassium carbonate is obtained from a number of very different materials. The greatest quantity is still produced from wood and other plant ashes, as well as from the residues of the molasses of beet sugar after distillation, wine, lees, and various kinds of sea weed. It is also obtained from the suint of the wool of sheep. Large quantities of potash have been recently prepared from potassium sulphate by Leblanc's process; while, on the other hand, the preparation of potash from feldspar and similar rocks has ceased to be of importance since the discovery of the potash deposits at Stassfurt and Kalucz. Attempts have been made of late, but without success, to prepare potassium carbonate direct from potassium chloride.

Potash from Wood Ashes.—Plants contain potassium combined with different acids, amongst which are a great number of vegetable acids that yield carbonic acid when the plants are incinerated. Only a very insignificant portion of the potassium carbonate found in the ashes of plants is contained in the plants as such before incineration.

The amount of potassium carbonate yielded by the ashes of different plants varies considerably. The following table by Höss gives the total ash yielded by 1000 parts of the undermentioned kinds of wood, and the corresponding amount of potassium carbonate yielded by the ashes.

	Ash.	Potash.
Pine	3·4	0·45
Beech	5·8	1·27
Ash	12·2	0.74
Oak	13·5	1·50
Elm	25·5	3·90
Willow	28·0	2·85
Vine	34·0	5·50
Fern	36·4	4·25
Wormwood	97·4	73·00
Fumitory	219·0	79·00

The different parts of the same plant yield upon incineration an ash of different quality, and consequently with a different percentage of potash. Thus Saussure obtained from the ash from different parts of the oak the following relative proportions of potash, the trunk wood being taken as unit:—

Trunk wood	1
Leaves and bark	36
Bark	30
Branches freed from bark	29
Sap-wood	2

The ash of plants contains other salts besides potassium carbonate, especially potassium sulphate and potassium silicate, together with considerable quantities of carbonates, sulphates, phosphates, silicates, and chlorides of calcium and magnesium, as well as small quantities of the corresponding salts of sodium, and traces of ferric oxide and manganese oxide; also sand and clay, and a small quantity of unburnt organic substance.

In preparing the ash, either entire trees or the leaves and twigs only are burnt, according as the secondary object in view is to clear the land or to make use of the wood. Wood ash is obtained by burning the wood on the spot; cinder ash is the waste product obtained when wood is used as fuel.

Adulterations of the wood ashes with substances such as turf, brown coal, coal, etc., are determined by the taste. The worth of an ash (in its potash contents) is generally roughly determined by the taste.

Lixiviation of the Ash.—The lixiviation of the ash has for its object the solution of the potassium carbonates; but a number of other substances are also dissolved which render the potassium carbonate impure. Before the actual lixiviation, the ash is either placed in steeping tubs, or spread upon a smooth floor sprinkled with water, and stirred so as to secure an equal moistening of the whole. After this operation the ash can be more tightly packed in the lixiviating vessels, and it is exposed for some

time to the action of the atmosphere, by which means a portion of the dissolved potassium silicate is converted into carbonate.

The lixiviating apparatus consists of three tubs, as represented by fig. 131, with perforated false bottoms (*c*) and outlet pipes (*a*). The perforated bottom is covered with a layer of straw, upon which the moistened ash is placed and stamped in; the space above the ash (about one-third of the tub) is then filled with water. The water, penetrating through the ash, dissolves out the soluble constituents, and the solution flows out through the outlet pipes below into settling tanks. The ash is again treated with water, and the liquor thus obtained is used for lixiviating fresh portions of ash in the second tub. A third supply of water to the first tub dissolves out the last traces of soluble constituents, and the dilute liquor is used for the second lixiviation of the second tub, then for the first lixiviation of a fresh quantity of ash in the third tub. After three lixiviating operations the tubs are emptied and recharged with fresh ash.

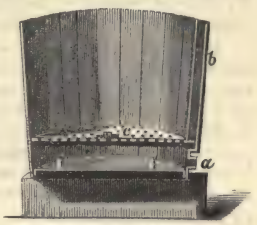


FIG. 131.

Instead of tubs, square brickwork vessels may be used, perforated at the bottom, three or four being placed together.

The undissolved residue in the lixiviating vessels consists essentially of calcium carbonate, clay, and sand, together with considerable quantities of calcium phosphate (according to Wolff about 11 per cent.), on account of which the residue forms a valuable manure.

Boiling down the Liquor.—This operation is carried out in a shallow cast-iron pan, fresh liquor being constantly added in proportion as the water evaporates, until a drop taken out and placed upon a cool metal plate solidifies to a crystalline mass; the fire is slackened, and the gradually solidifying residue in the pan is gently heated to dryness.

In order to avoid the adhesion of the potash to the bottom of the pan during the drying operation, the mass should be well stirred.

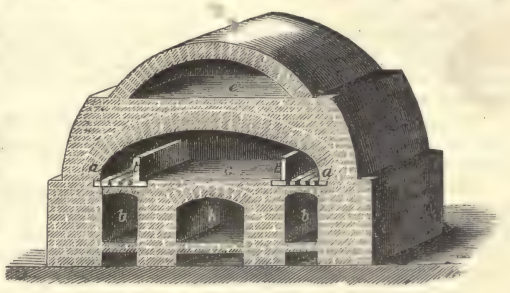


FIG. 132.

In some works the liquor is only evaporated so far that, upon cooling, potassium sulphate crystallises out, and then the mother liquor from the crystals is evaporated to dryness.

The product obtained by the above operation is called raw or crude potash. It is in most cases coloured brown by an admixture of organic substance, and it contains about 20 per cent. of water.

Calcination of Crude Potash.—The object of this operation is the removal of water and organic substance. Care must, however, be taken to avoid heating the potash too much, otherwise it may melt, and some of the organic substance become imbedded in the mass so as to prevent its being burnt; besides this, the melted potash would dissolve out silicic acid from the hearth. The calcination is carried out in reverberatory furnaces heated with wood, the flame passing over the potash from the furnaces (*a a*, fig. 132) on both sides of the calcination hearth (*c*). At first the potash froths up owing to escape of water; it then becomes black from the separation of carbon, and finally, when the organic substance is completely burnt, the potash assumes a white or greyish-white colour. The mass is stirred at intervals during the operation so as to secure uniform heating.

Formerly the calcination was carried out in iron pots, and on this account the product was termed potash; but with the present extensive consumption of potash this plan would be too inconvenient.

ROCK ASH.—This substance is imported from America, and in preparing it caustic lime is added in the lixiviation of the ashes. In this way caustic potash is formed. Owing to the facility with which caustic potash melts, the calcination of rock ash cannot be carried out in reverberatory furnaces, and, therefore, the liquor is evaporated in

pans until a drop solidifies to a hard mass upon cooling, and then the concentrated liquor is poured into iron boxes, where it solidifies.

Pearlash.—This substance, also imported from America, is prepared by lixiviating ordinary crude potash with water, drawing off the liquor when clear, evaporating, drying, and calcining. Since potash absorbs moisture from the air, it requires to be packed in well-closed vessels.

Potash from Molasses.—Beet molasses contains a considerable amount of inorganic salt, especially potash salts, which can be profitably extracted. The molasses is first fermented, and its sugar converted into alcohol, which is distilled off. The residue, after distillation, is then concentrated in the cooler part of a reverberatory furnace, the hearth of which is formed by an iron pan, and afterwards calcined in the hotter part of the furnace. The mass thus obtained is of a dark colour, owing to the presence of carbonised substance; it contains about 25 per cent. of insoluble substance, and 75 per cent. of soluble salts, including 30 to 35 per cent. of potassium carbonate and 18 to 20 per cent. of potassium chloride. This mass is submitted to a methodical lixiviation, and the liquor thus obtained is treated for potash either in the ordinary way by evaporating, drying, and calcining, or by fractional evaporation and crystallisation, to obtain potassium sulphate, a mixture of potassium sulphate and sodium carbonate, besides potassium chloride, sodium carbonate, a double compound of soda and potash, and lastly tolerably pure potash, by evaporating the mother liquor to dryness and calcining.

At some places other methods are adopted for concentrating the residue from distilled molasses; thus, for instance, it is often heated by steam in wooden vessels, or boiled down in iron pans, heated from below.

The molasses residue is often so strongly calcined that it has a white or greyish-white appearance. The insoluble residue obtained after lixiviating the calcined mass is used as manure.

Potash from Wine Lees.—The quantity of potash obtained from this source is very insignificant. The residue obtained in preparing 'after wine' (*vide* Wine) is dried, calcined, and lixiviated, the lye thereby obtained being treated for potash in the ordinary way.

Potash from Sea-Weed.—In treating sea-weed, for kelp or varec, salts are separated which contain potassium carbonate. They only require lixiviation in order to obtain from them a pure potash.

Potash from Suint.—The greasy exudation from the skin of sheep contains a large amount of potash salts, and the water used for washing wool is worth working for potash salts. In localities where woollen manufactures are carried on, considerable quantities of potassium sulphate and potassium carbonate are obtained from this source.

For this purpose the wash water is evaporated to dryness, and the residue heated in gas retorts; the gas evolved is washed to separate ammonia, and is then used as illuminating gas. The carbonaceous residue in the retorts is lixiviated, and the liquor submitted to fractional evaporation and crystallisation, so as to obtain successively potassium sulphate, potassium chloride, and a mother liquor, which, when evaporated to dryness and calcined, yields comparatively pure potash.

Potash from Potassium Sulphate.—The preparation of potassium carbonate in this way is conducted in the same manner as the preparation of sodium carbonate by Leblanc's method by heating it with carbon and chalk. The potassium sulphate is first reduced to potassium sulphide, according to the equation:

$$K_2SO_4 + 4C = K_2S + 4CO.$$

The potassium sulphide then reacts upon the chalk, forming calcium sulphide, and potassium carbonate, according to the equation:

$$K_2S + CaCO_3 = CaS + K_2CO_3.$$

Owing to the volatility of potassium sulphide, its formation in this process involves great loss of potash.

The insoluble residue left, after lixiviating the calcined mass, consists essentially of calcium sulphide, from which the sulphur is recovered according to one of the methods mentioned in a former chapter (*vide* page 100).

Potash from Schönite.—Schönite ($K_2SO_4 + MgSO_4$) also admits of being treated for potash according to Leblanc's method of preparing soda, and in all cases where potassium sulphate is to be converted into potassium carbonate, the presence of some schönite is advantageous, since the magnesia produced from the magnesium sulphide renders the mass porous, and facilitates the lixiviation.

Many methods have been proposed for converting potassium chloride into carbonate; but none of them have yet proved successful.

Refining.—One method of purifying crude potash consists in treating it with about three-fourths of its weight of pure cold water. The more soluble constituents, such as potassium carbonate and potassium hydrate, are thus dissolved, while the less soluble, such as potassium sulphate, remain for the most part undissolved. The clear solution drawn off and evaporated to dryness yields a residue consisting of tolerably pure potassium carbonate, contaminated with small quantities only of potassium chloride, silicate, and sulphate.

Another method consists in treating crude potash with two parts of water in an iron cauldron, with the application of a gentle heat; then either filtering off or decanting the solution, and evaporating it until potassium sulphate crystallises on cooling. The mother liquor is then decanted off and concentrated until potassium carbonate separates in small crystals upon cooling. The mother liquor contains potassium chloride and potassium silicate. This method affords a very pure potash.

In this country crude pearlash is refined for the preparation of flint glass by mixing it with sawdust and calcining the mixture in a reverberatory furnace. The carbonic acid, formed by the combustion of the sawdust, converts the potassium hydrate and potassium sulphide in the crude potash into potassium carbonate. The mass is then lixiviated with cold water, the liquor left to settle, the residue drawn off, again evaporated to dryness, and the residue calcined in a reverberatory furnace. The calcined mass is again lixiviated, the liquor evaporated to dryness, and the residue calcined as before. The calcined product of this operation is once more lixiviated, the liquor concentrated by evaporation until potassium sulphate crystallises out; the mother liquor is then further concentrated until fine crystals of potassium carbonate separate on cooling. The crystals are removed from the mother liquor, and consist of very pure potash.

The value of crude potash is dependent upon the amount of potassium carbonate and caustic potash it contains. For certain purposes, however, the other constituents of crude potash are not without value. Thus, for instance, in the manufacture of alum both potassium chloride and potassium sulphate are used.

Uses.—Although the use of potash for industrial purposes is in many cases supplanted by the cheaper substance soda, it still finds extensive employment.

Potassium carbonate is used in the manufacture of potassium nitrate, Bohemian glass, for preparing smalt, alum, potassium cyanide and chlorate, as well as other potassium salts; it is also used as a manure, and in dye and bleaching works, etc.

ACID POTASSIUM CARBONATE.

Formula $KHCO_3$. Molecular Weight 100·1.

This salt, commonly called potassium bicarbonate, is a white crystalline substance very much less soluble in water than the normal carbonate, as shown by the following table by Poggiale:

100 parts of water at	0°	dissolve	19·61	parts of the salt.
„	10°	„	23·33	„
„	50°	„	37·92	„
„	70°	„	45·24	„

The solution does not materially affect the colour of red litmus or turmeric paper. The crystals are rhomboidal prisms. They are anhydrous; by heat the salt is decomposed, giving off water and carbonic dioxide; this decomposition taking place to some extent even when a solution of the salt is boiled.

Acid potassium carbonate is prepared by passing carbonic dioxide into a solution of potassium carbonate in water; it is used chiefly for medicinal purposes.

POTASSIUM SULPHATE.

Formula K_2SO_4. Molecular Weight 174·2.

Characters.—Potassium sulphate crystallises in four-sided prisms or double six-sided pyramids belonging to the trimetric system. It is sparingly soluble in cold water, rather more so in hot water, and it is quite insoluble in alcohol. The addition of alcohol to an aqueous solution of potassium sulphate causes the complete precipitation

of the salt. Potassium sulphate is remarkable for the facility with which it combines with other sulphates to form double salts. A few of these double sulphates occur naturally, as, for instance, polyhalite, kainite, and schönite, found at Stassfurt. Nearly all soluble sulphates form double salts with potassium sulphate.

Preparation.—The conversion of potassium chloride into sulphate by means of sulphuric acid has been largely carried out of late years. The process is similar to Leblanc's soda process. Potassium chloride is placed in a sulphate furnace, and covered with sulphuric acid, the escaping hydrochloric acid being condensed and collected. The potassium sulphate is then generally converted into carbonate by Leblanc's method.

According to Grüneberg's method of preparing potassium sulphate from potassium chloride and artificial schönite, potassium chloride and kieserite are first dissolved together in hot water; the change that takes place is represented by the following equation:

$$\underset{\text{Kieserite}}{3KCl + 2MgSO_4} = \underset{\text{Schönite}}{MgSO_4 + K_2SO_4} + \underset{\text{Carnallite}}{(KCl + MgCl_2)}.$$

The liquor is then submitted to a process of fractional crystallisation, so as to separate the schönite from the carnallite. The schönite is then dissolved in hot water, the solution brought to a concentration corresponding to sp. gr. 1·321, and poured over finely sifted potassium chloride, with which it is allowed to remain in contact, until the temperature has sunk to 40°. At this point the greater part of the potassium chloride is converted into sulphate, according to the equation:

$$\underset{\text{Schönite}}{3KCl + MgSO_4 + K_2SO_4} = 2K_2SO_4 + \underset{\text{Carnallite}}{(KCl + MgCl_2)}.$$

The mother liquor poured off from the potassium sulphate yields a further crop of this salt, when cooled to a lower temperature, and by concentration it yields first schönite and then carnallite. The potassium sulphate thus obtained is freed from mother liquor by means of a centrifugal machine, and is then very pure (95 per cent.)

Grüneberg also treats schönite with a cold solution of potassium chloride of sp. gr. 1·160, by pouring and re-pouring the cold solution over the schönite, until the potassium chloride has been almost entirely converted into potassium sulphate. The liquor then contains chiefly carnallite, schönite, and potassium chloride, which are extracted by evaporation and fractional crystallisation.

Potassium sulphate is obtained in considerable quantities as a by-product in the preparation of a number of salts, as in the treatment of the mother liquors obtained in the preparation of common salt from sea water and brine springs (see Sodium Chloride); in the preparation of iodine (page 181); in the preparation of potash from the ashes of plants; in the preparation of nitric acid from potassium nitrate and sulphuric acid (page 45), etc.

Potassium sulphate has also of late been obtained from kainite, by treating it with water, which decomposes it into magnesium chloride and schönite; the schönite crystallises out, and is treated for potassium sulphate, according to one or other of the methods above given.

Uses.—Potassium sulphate is considerably used as a manure, also in alum and glass works. A recent application of the salt consists in treating it for potash by Leblanc's method.

ACID POTASSIUM SULPHATE.

Formula $KHSO_4$. Molecular Weight 136·1.

This salt is commonly called potassium bisulphate, and is intermediate in composition between potassium sulphate and hydric sulphate; it melts at 197°, dissolves in twice its weight of cold water and in half its weight of water at 100°; the crystals have the form of flattened rhombic prisms and are anhydrous. At a high temperature water is given off and then sulphuric oxide, leaving neutral potassium sulphate. Acid potassium sulphate is often obtained as a by-product in chemical operations, and it is used sometimes as a flux in cases where the action of an acid oxide at a high temperature is required, as in the decomposition of some aluminous minerals for analytical purposes.

ACID POTASSIUM TARTRATE.

FORMULA $KHC_4H_4O_6$. MOLECULAR WEIGHT 188·1.

This salt, which is known in the purified state as potassium bitartrate or cream of tartar, occurs in commerce in an impure form as tartar or argol, the latter consisting of the crystalline crust deposited from grape juice during its fermentation, upon the sides of the vats or wells in which the process takes place, while the former is produced from it by extraction with hot water and crystallisation.

Argol exhibits a wide range of composition, the amount of tartaric acid ranging, according to Warington, from 40 to 70 per cent. Pure bitartrate contains 79·7 per cent. tartaric acid. Argol often contains small particles of sulphur, which originate from the sulphuring of the casks.

Tartar contains from 70 to 77 per cent. of tartaric acid, and, according to Warington, from 1·5 to 44·5 of this exists in the state of calcium tartrate in the best kinds of tartar, which come from Southern Italy and Messina. According to Scheurer-Kestner, some kinds of French and Hungarian tartar contain calcium tartrate in much larger amount, as much as 46 per cent. Tartar of inferior quality contains, besides potassium bitartrate and calcium tartrate, small amounts of carbonates, sulphates, phosphates, and silicates, together with organic substances.

The purified salt as usually met with forms colourless crystalline masses; it is but slightly soluble in water, requiring 240 times its weight of cold water and 15 parts of boiling water for solution; it is insoluble in alcohol, and its solubility in water is reduced by the presence of a small amount of alcohol. It is on this account that the salt is deposited from grape juice, as in the process of fermentation the sugar it contains is converted into alcohol.

Uses.—Potassium bitartrate is frequently used as a mordant in dyeing wool and for preparing pure potassium carbonate; when mixed with alum and chalk it forms a good powder for cleaning plate. Black flux, consisting of potassium carbonate mixed with carbon, is prepared by heating the bitartrate to redness in a close crucible. White flux, consisting of potassium carbonate, is obtained by igniting a mixture of the bitartrate and potassium nitrate.

ACID POTASSIUM OXALATE.

FORMULA KHC_2O_4. MOLECULAR WEIGHT 128·1.

This salt, which is commonly called Salt of Sorrel, occurs in the juice of various species of *Rumex* and *Oxalis*; it is obtained either by crystallisation from the clarified juice of these plants, or by partially neutralising oxalic acid with potassium carbonate. It forms transparent crystals containing one molecule of water of crystallisation; it has a sour taste, and is sparingly soluble in water, requiring 14 times its weight of cold water and 4 parts of boiling water.

Acid potassium oxalate is used for scouring metals and for removing ink stains or iron mould, its action in this case being due to the formation of a double potassium and iron oxalate, which is soluble in water.

Another salt, containing a larger proportion of oxalic acid, is sometimes met with in commerce as salt of sorrel; it is a tetroxalate or quadroxalate, the composition of which is represented by the formula $KH_3.2C_2O_4.2aq.$

POTASSIUM NITRATE (SALTPETRE).

FORMULA KNO_3. MOLECULAR WEIGHT 101·1.

History.—The salt which the Greeks and Romans called 'nitrum' was in all probability potassium carbonate, and not potassium nitrate, as was at one time supposed. The earliest accounts of saltpetre are of more recent date. In the eighth century mention is made by Geber of a salt, 'sal petræ,' which was probably ordinary saltpetre. Magnus Græcus, to whom we are indebted for the first account of the preparation of gunpowder, must also have been acquainted with this salt. It was mentioned later on in the thirteenth and fourteenth centuries, generally under the name of nitrum, in the writings of Albertus Magnus, Roger Bacon, and Raymond Lully. Boyle, in 1667, was the first to state that saltpetre contains fixed alkali and nitric acid.

Occurrence.—Saltpetre occurs naturally in considerable quantities. It is often found as an efflorescence upon the surface of the ground, as in the neighbourhood of the Ganges in India, in the island of Ceylon, in Peru, Chili, Egypt, Persia, Hungary, etc. The crust of salt, which is often as much as $\frac{1}{2}$ in. in thickness, is generally formed after the rainy season is over. In other districts, saltpetre is found at some distance below the surface of the earth, in layers of varying thickness, mixed with clay and other impurities. Saltpetre is also found in caves, as in Ceylon, in Kentucky, in North America, in Apulia, in Naples, etc. Saltpetre occurs in small quantities in Germany, in the red sandstone near Göttingen, in the Tuffkalk caves near Würzburg; it is found in France, in the chalk at Roche-Guyon, Angoulême, etc.; in Portugal near Lisbon; and in Russia in the Ukraine.

Composition and Properties.—The composition of potassium nitrate is represented by the formula $\left.\begin{matrix}NO_2\\K\end{matrix}\right\}O$. It is often called prismatic saltpetre or potash saltpetre, to distinguish it from cubic or Chili saltpetre, which is sodium nitrate. Potassium nitrate crystallises in long six-sided prisms belonging to the trimetric system. The crystals often contain cavities filled with mother liquor, which renders the saltpetre impure. Potassium nitrate possesses a strong saline and cooling taste. When gently heated it melts to a mobile liquid, which solidifies on cooling. A stronger heat causes decomposition; oxygen is evolved, and potassium nitrite remains. The application of a still stronger heat causes decomposition of the potassium nitrite, nitrogen and oxygen escaping, while a mixture of potash and potassium peroxide remains behind. Potassium nitrate is not very soluble in water at the ordinary temperature; but its solubility increases very rapidly with rise of temperature. According to Gay-Lussac the solubility of this salt in 100 parts of water at different temperatures is as follows:—

At 0°	13·32 parts
„ 11°·67	22·23 „
„ 24°·94	38·40 „
„ 45°·10	74·66 „
„ 65°·45	125·42 „
„ 97°·66	236·45 „

The following table by Gerlach shows the relation between the percentage of saltpetre in aqueous solutions of the salt, at a temperature of 15°, and the specific gravity of such solutions:

Specific Gravity	Percentage of Saltpetre	Specific Gravity	Percentage of Saltpetre
1·00641	1	1·07905	12
1·01283	2	1·08595	13
1·01924	3	1·09286	14
1·02566	4	1·09977	15
1·03207	5	1·10701	16
1·03870	6	1·11426	17
1·04534	7	1·12150	18
1·05197	8	1·12875	19
1·05861	9	1·13599	20
1·06524	10	1·14361	21
1·07215	11	1·14427	21·074

Heated with other bodies, saltpetre exerts upon them a powerful oxidising action; carbon is oxidised to carbonic acid, sulphur to sulphuric acid, and most of the metals to their respective oxides, etc.

Preparation.—Saltpetre is obtained in three ways: α, by lixiviation of the earth containing naturally formed saltpetre; β, by means of nitre plantations; γ, by decomposing Chili saltpetre with potassium chloride.

Natural Saltpetre.—The method adopted for the treatment varies with the district where it is found. In India the saltpetre earth is made up into large heaps, where, under constant stirring of the mass, it is exposed for some time to the action of the air, the heaps being protected by sheds during the rainy season. After the earth has lain sufficiently long, it is brought into macerating vessels, where it is treated with water, and after a few hours the lye is drawn off, allowed to clear in large basins, and then evaporated in suitable pans until a crust of saltpetre forms on the surface.

The lye is then drawn off into shallow crystallising vessels, where it deposits crystals of crude saltpetre.

The same method is adopted in Egypt, Persia, and South America.

Saltpetre occurs in Ceylon in caves situated in a rock consisting chiefly of dolomite mixed with felspar, quartz, and mica. To obtain the saltpetre the rock is excavated from the sides of the caves, broken up, and mixed with wood ashes, and the mixture lixiviated. Crude saltpetre is then obtained by evaporating the lye thus obtained, and allowing it to crystallise in earthen pots. The addition of wood ashes is intended to convert the magnesium nitrate into potassium nitrate by means of the potassium carbonate contained in them.

In Hungary, at Nagy-kallo, Nyiregyháza, Debreczin, etc., the saltpetre earth is scraped together with a kind of spade, or by means of a peculiarly constructed plough, the saltpetre being then obtained by lixiviation and evaporation of the lye.

The amount of saltpetre contained in the different saltpetre earths varies considerably. Saltpetre earth from Tirhoot in Bengal contains from 8 to 9 per cent. of potassium nitrate, and from 3 to 4 per cent. of calcium nitrate. The saltpetre rock of Ceylon contains, according to J. Davy, 2·4 per cent. of potassium nitrate, and 0·7 per cent. of magnesium nitrate. Ragsky's analyses of the saltpetre earths of Hungary represent the latter as containing from ½ to 2½ per cent of potassium nitrate.

Plantations.—This method of preparing saltpetre was formerly far more general than at the present time, it having been found that the importation of naturally formed saltpetre, as well as the manufacture of potassium nitrate by conversion from Chili saltpetre, are cheaper sources.

Theory of the formation of Saltpetre.—The formation of nitric acid takes place when decaying animal substances are exposed to the action of moisture and atmospheric air in contact with materials containing much potash or carbonate of lime—for instance, marl, old building rubbish, road scrapings, etc., or vegetable substances containing potash, such as the leaves and stems of the potato, beet, sunflower, nettles, etc. By the decay of the animal substances, ammonia is first formed, and this is gradually oxidised. In saltpetre plantations these materials are arranged in ridges or heaps of a pyramidal shape, exposed in all directions to the action of atmospheric air, the circulation of which is promoted by layers of straw. The heaps are protected from rain by roofs. The ground upon which these heaps are built is first covered with clay well rammed down, so as to prevent nitrates from being washed away by the penetration of water. The heap is watered at intervals with lant (stale urine), which affords a supply of nitrogenous material as well as water. These heaps are generally allowed to remain at rest for a period varying from one to three years. Tests are made from time to time to ascertain the point of ripening, when the formation of saltpetre is at an end. A cubic foot of the earth ought to yield about 2½ ozs. of saltpetre.

Preparation of the Crude Lye.—The ripe earth is broken up with mallets or hammers, and after being sifted to separate lumps, the finely divided earth is lixiviated in such a manner that dilute solutions obtained from portions of earth that have already been once washed are used for lixiviating fresh portions of earth. The lixiviating vessels are either tubs with perforated false bottoms upon which the earth is strewn, or shallow wooden boxes widening towards their upper part, and furnished near the bottom with lateral holes for running off the lye. The holes can be closed with plugs, and to prevent their being stopped by pieces of earth, they are protected internally with perforated boards. Two of these vessels are placed side by side, and when filled with earth, water, in quantity equal to half the volume of earth, is poured in, so as just to cover the earth. After about twenty-four hours the lye is drawn off by removing the plugs, and the residue in the lixiviating vessel is treated with a fresh quantity of water, the lye from this second lixiviation (if it does not contain over ten per cent. of saltpetre) being used for lixiviating fresh portions of earth. A third lixiviation of a quantity of earth yields a lye which is also employed for the lixiviation of fresh portions of earth.

Other kinds of lixiviating apparatus, such as those used in alkali works, may be very conveniently used for the lixiviation of saltpetre.

Breaking the Raw Lye.—Since in the construction of saltpetre plantations calcium carbonate is nearly always the material used for supplying the base, the nitric acid in the raw lye is to a great extent in combination with calcium. Besides calcium nitrate, the lye contains magnesium and potassium nitrates, as well as small quantities of calcium, magnesium and potassium chlorides, together with organic substances and salts of ammonia. The conversion of the calcium or magnesium nitrate into the corresponding potassium salt is an operation termed technically breaking the lye. For this purpose potassium carbonate or potash is added to the lye, which re-acts with the

calcium nitrate, forming insoluble calcium carbonate and potassium nitrate, according to the following equation:

$$Ca2NO_3 + K_2CO_3 = CaCO_3 + 2KNO_3.$$

Magnesium nitrate is likewise decomposed in a similar manner, while the calcium and magnesium chlorides of the crude lye yield, with potassium carbonate, potassium chloride and the carbonates of calcium and magnesium respectively.

The operation is carried out as follows. A small quantity of potash is dissolved in double the quantity of water, and a measured quantity of the raw lye is treated with this solution until all the calcium and magnesium are precipitated. From the quantity of potash solution required in this test, the quantity required for the whole of the crude lye is calculated, and mixed with the lye in large wooden tubs. After standing a short time the precipitate settles, and the clear lye above is drawn off by taking out plugs at different heights along the sides of the tubs.

Other materials used in the place of potash for breaking the lye are potassium sulphate, potassium chloride, and sodium sulphate. In this case, however, the magnesium salts contained in the crude lye are decomposed before adding the potash salt, by the addition of milk of lime, which throws down magnesia as a precipitate. The calcium is then precipitated as sulphate.

In the next operation of boiling down, the lye is concentrated to such an extent that the potassium and sodium chlorides separate for the most part from the hot solution, while the crude saltpetre crystallises out on allowing the lye to cool.

Fig. 133 represents an apparatus for boiling down the crude lye. The lye is brought into the hemispherical pan BB' and heated to the boiling point by means of a fire A. The hot air from the fire plays first of all upon the bottom of the pan, then passes round it and underneath another pan, where the lye is heated, and escapes eventually into a chimney. In some places the flue gas is made to heat a pan for drying the saltpetre. When the crude lye begins to boil, the previously dissolved calcium carbonate or sulphate are first separated, the particles suspended in the liquid being carried upwards at the sides by the boiling motion of the liquid, and falling to the bottom in the middle of the vessel. In order to prevent this precipitate from adhering to the bottom of the pan, as well as for the convenience of removing it, a cullender (c), supported by a chain (*d*) running over pulleys (*d' d''*), is placed at the bottom of the pan; this catches the precipitate, and is occasionally drawn out and emptied upon a strainer (*f f'*), which allows the adherent lye to flow back into the evaporating pan. The scum formed during the boiling down is due to organic substances; this is removed by means of a perforated ladle. Further boiling down causes separation of the potassium and sodium chlorides that are collected apart. In spite of the care taken in allowing the adherent mother liquor to drain back into the pan from the first precipitates, they still retain considerable quantities of saltpetre. They are therefore placed in baskets and immersed in boiling water, this operation being repeated with fresh portions until a lye is obtained saturated with saltpetre, from which saltpetre crystallises out upon cooling. In proportion as the crude saltpetre lye evaporates, new portions of lye are run in, until the further formation of cubic crystals of the chlorides of potassium and sodium ceases, and a fine crystalline film of saltpetre is formed. A portion of the lye tested at this point by dropping it upon a cold surface, solidifies at once.

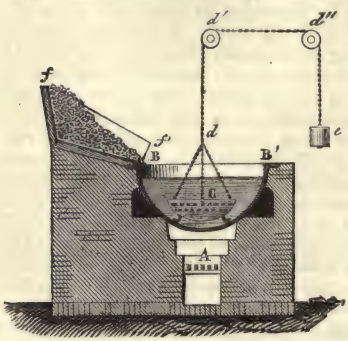


FIG. 133.

When this point is reached the lye is run off into large settling vats, where it is allowed to remain about six hours, in order to deposit all suspended impurities. When the temperature of the mass has cooled down to 60° the clear lye is drawn off into crystallising vessels, where it cools in about a couple of days, and the crude saltpetre crystallises out. The mother liquor, separated from the salt, is returned to the evaporating pans, but eventually it becomes so concentrated and contains so large an amount of foreign salts, and is so much coloured with organic substances, that it is either thrown away or added to the saltpetre earth.

According to the purpose for which saltpetre is to be used it is crystallised in large or small crystals. When required for the manufacture of nitric acid, it is made to crystallise in a very minute state of division, by continually stirring the hot lye

during crystallisation; but when it is required for subsequent refining, crystallisation is allowed to go on slowly, so that large crystals may be obtained.

Crude saltpetre may contain as much as twenty-five per cent. of impurities, amongst which the potassium and sodium chlorides constitute an important part; it also contains small quantities of sodium, calcium, and magnesium sulphates, together with a small quantity of organic matter.

Refining of Crude Saltpetre.—In order to separate impurities, the crude saltpetre is placed in large iron or copper vessels, and dissolved with the application of a moderate heat in about half its weight of water. This solution is made to boil, and a further addition is then made of one-and-a-half times as much more raw saltpetre. The water present suffices for the complete solution of all the potassium nitrate, but leaves a considerable quantity of the comparatively less soluble potassium and sodium chlorides undissolved, which is removed with perforated ladles, while at the same time the organic scum is skimmed off. When calcium and magnesium salts are present, they are got rid of by adding to the lye a sufficient quantity of potassium carbonate. The complete removal of organic matter is effected by diluting the lye with about half its volume of water, and adding a hot solution of glue. A fresh scum is thus formed containing all the organic substance combined with gelatin, and this is skimmed off. When the formation of scum has entirely ceased, the lye is left at rest for about twenty-four hours, after which time it will have cooled down to about 90°, and become clear. It is then drawn off into shallow cast-iron crystallising vessels, the bottoms of which slope towards the centre. The liquid is constantly stirred while cooling, so that very small crystals may be formed (saltpetre flour), which are purer than large crystals, since they do not contain enclosed mother liquor. The saltpetre flour is raked out as soon as formed, and the mother liquor is drawn off from the centre of the pans, and used for dissolving fresh portions of crude saltpetre.

Washing the Saltpetre Flour.—The object of this operation is to remove from the crystals adhering mother liquor, as well as to effect the solution and removal of any chlorides separated with the saltpetre. For this purpose wooden washing vats are employed about 10 feet long and 3 feet wide, narrower at the bottom than at the top. They are furnished with a perforated bottom upon which the saltpetre flour is placed, and covered with a concentrated solution of pure saltpetre, with which it is allowed to remain in contact for three hours. The liquor is then drawn off, and the saltpetre washed with an equal quantity of water, the operation of washing with a solution of pure saltpetre and then with water being repeated twice or more until a portion of the wash liquor when tested ceases to give a perceptible precipitate with silver nitrate. The first portions of wash liquor are used for dissolving fresh portions of raw saltpetre, the last purer portions for treating fresh quantities of saltpetre flour. The saltpetre flour, after having been in this way rendered perfectly pure, is allowed to remain a few days still in the washing tanks, after which it is taken out and dried.

Drying the Saltpetre.—The drying of the saltpetre is effected in various ways. It is sometimes dried in pans at a moderate temperature, sometimes in a current of hot air upon drying tables covered with linen. In some places the saltpetre is melted and cast into sticks or blocks. Occasionally it is again dissolved in water and converted into large crystals by a process of slow crystallisation.

The loss sustained by refining amounts to about 25 per cent. of the total quantity of potassium nitrate contained in the raw saltpetre.

Refining of Indian Saltpetre.—The method of refining the crude saltpetre from India is essentially the same as that just described; the loss is, however, not more than from 5 to 7 per cent., since the raw material is less impure.

Preparation of Potassium Nitrate from Chili Saltpetre.—The conversion of Chili saltpetre or sodium nitrate into the corresponding potassium salt depends upon the fact that concentrated solutions of potassium chloride and sodium nitrate mutually decompose when heated, forming sodium chloride and potassium nitrate according to the equation:

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

The operation is carried out as follows: An aqueous solution of potassium chloride is prepared of a specific gravity of 1·200 to 1·210 in a large cast-iron cauldron holding about 880 gallons, and mixed with an equivalent quantity of Chili saltpetre; the whole being heated until the lye has a specific gravity of 1·500. In estimating the quantities of the respective salts, it must be remembered that commercial Chili saltpetre does not contain more than from 90 to 96 per cent. of sodium nitrate, and that

commercial potassium chloride, according to the source from which it is obtained, contains only from 60 to 96 per cent. of potassium chloride. The sodium chloride separated during the boiling of the lye is removed either with rakes or cullenders and placed to drain in a wooden strainer above the boiling pan. The crystals of sodium chloride are washed with a small quantity of water, which is also allowed to run back into the boiling pan. As soon as the lye shows a specific gravity of 1·500, it is allowed to stand a short time to get clear, and is then run into shallow crystallising vessels, where the crystallisation is generally complete in about twenty-four hours. During the crystallisation the whole is stirred so as to obtain very small crystals. When the crystallisation is complete the mother liquor is drawn off and the crystals placed in wooden tanks furnished with perforated false bottoms, where they are just covered with water and allowed to remain thus for about eight hours. The lye thereby formed, containing the greater part of the impurities present in the saltpetre, such as sodium chloride, sodium nitrate, potassium chloride, etc., is drawn off, this operation being repeated once or twice, according to the degree of purity required for the saltpetre. The mother and wash liquors are used for dissolving fresh portions of potassium chloride.

Wöllner's Method.—According to this method Chili saltpetre is converted into potassium nitrate by means of potassium carbonate. Solutions of Chili saltpetre and potassium carbonate, each of a concentration of sp. gr. 1·380, are allowed to flow in the requisite proportions into large metal pans, where the liquor is heated till it has a specific gravity of 1·462 to 1·490. The sodium carbonate, which continually separates, together with much sodium nitrate, during the heating, is removed and placed in filtering boxes consisting of sheet-iron cylinders, with perforated false bottoms. These cylinders admit of being hermetically closed, and they are furnished at the upper part with cocks for admitting steam, while at the lower part there are taps for running off the lye. Upon passing steam into the cylinders filled with sodium carbonate containing sodium nitrate, both salts are dissolved, but the potassium nitrate solution being specifically heavier than the solution of sodium carbonate, in the proportion of sp. gr. 1·462 or 1·490 to sp. gr. 1·299, sinks to the bottom of the cylinder, and is drawn off first, the soda lye afterwards. The lye, containing potassium nitrate, is run back into the boiling pan, and this operation is continued until pure potassium nitrate crystallises out upon cooling the lye, for which purpose it is drawn off into crystallising vessels.

A modification of the above process consists in treating the sodium carbonate resulting from the decomposition of sodium nitrate and potassium carbonate with hydrate of calcium before the separation, whereby the soda is converted into caustic soda, and the calcium carbonate thereby formed settles at the bottom of the vessel as an insoluble precipitate. The lye is drawn off from the latter and evaporated, whereupon saltpetre crystallises out, and caustic soda remains dissolved, which is then obtained by further evaporation.

Chili saltpetre may be also converted into ordinary saltpetre by treating it with caustic potash, whereby caustic soda is obtained as a by-product. Another method consists in treating soda saltpetre with a solution of barium chloride, so as to form barium nitrate, which is sparingly soluble, and is precipitated in a very pure state. By treating the barium nitrate with potassium sulphate, insoluble barium sulphate is formed, and the lye contains potassium nitrate.

Testing of Potassium Nitrate.—In testing commercial saltpetre the chief thing to be ascertained is the percentage of pure potassium nitrate. The actual impurities are determined in the ordinary analytical way.

Austrian Saltpetre Test.—This test was introduced by Huss, and is based upon the fact that a definite quantity of water, at different temperatures, dissolves a definite quantity of potassium nitrate; and, further, that the quantity dissolved is in no way influenced by the presence of sodium or potassium chloride. Therefore, on dissolving a known quantity of saltpetre in a known quantity of water, potassium nitrate will crystallise out of the solution immediately the temperature is reduced below the point at which the potassium nitrate contained in the saltpetre sample forms a saturated solution with the water employed.

In making this test 40 parts of saltpetre are dissolved in 100 parts of water, at a temperature of 57°, the water evaporated during the process of dissolving being replaced; the solution is filtered off, and the vessel containing the filtrate is placed in cold water, the temperature at which potassium nitrate begins to separate being ascertained by means of a very delicate thermometer.

By reference to the following table constructed by Huss, the quantity of pure saltpetre that is dissolved in 100 parts of water may be read off, or the percentage of pure potassium nitrate contained in the sample of crude saltpetre tested.

Temperature at which the crystals begin to form	Amount of Potassium Nitrate dissolved in 100 parts of water	Percentage of Potassium Nitrate in the crude Saltpetre	Temperature at which the crystals begin to form	Amount of Potassium Nitrate dissolved in 100 parts of water	Percentage of Potassium Nitrate in the crude Saltpetre
10°·00	22·27	55·7	18°·12	30·36	75·9
10°·62	22·80	57·0	18°·75	31·09	77·7
11°·25	23·36	58·4	19°·37	31·83	79·6
11°·87	23·92	59·8	20°·00	32·50	81·5
12°·50	24·51	61·3	20°·62	33·36	83·4
13°·12	25·12	62·8	21°·25	34·15	85·4
13°·75	25·71	64·3	21°·87	34·96	87·4
14°·37	26·32	65·8	22°·50	35·81	89·5
15°·00	29·96	67·4	23°·12	36·70	91·7
15°·62	27·61	69·0	23°·75	37·61	94·0
16°·25	28·27	70·7	24°·37	38·55	96·2
16°.87	28·95	72·4	25°·00	39·51	98·8
17°·50	29·65	74·1			

Swedish Test.—A small quantity of the saltpetre to be tested is melted in a ladle and cast in moulds into pieces of about 1 inch thick. When cold these pieces, if pure, show when broken a coarsely rayed fracture; the greater the proportion of impurities contained in the crude saltpetre, the less distinct is this crystalline fracture, and it disappears altogether when 2½ per cent. only of sodium chloride is present.

Testing for Chili Saltpetre in samples of Crude Saltpetre. Wöllner's Method.—A portion of the sample to be tested is moistened with a little water and allowed to stand several hours. The sodium nitrate being most soluble, it dissolves completely, while comparatively little of the less soluble potassium nitrate dissolves. When the sample is placed in a small funnel and washed with a very small quantity of cold water, the filtrate will contain almost the entire quantity of sodium nitrate and very little potassium nitrate. The filtrate is then evaporated to dryness, and the residue treated as above, repeating this operation several times until the soda saltpetre is obtained in such a pure state that it may be recognised by its crystalline form (cubical rhombohedra piled up one on another) and the amount roughly estimated.

Pelouze's Method.—Pelouze determines the amount of saltpetre contained in crude saltpetre in the following way. A weighed quantity of pure iron wire is dissolved in sulphuric acid, the solution is mixed with a weighed quantity of saltpetre, and the whole heated. The nitric acid of the saltpetre is thus set free and oxidises a part of the ferrous sulphate formed by the action of the sulphuric acid upon the iron wire. The liquid is then poured into a beaker glass, cold distilled water added, and the quantity of iron present in the state of ferrous salt determined by titration with a solution of permanganate of potash.

Since it is easy to calculate the quantity of ferrous oxide obtained from the iron taken, the amount of ferrous oxide oxidised by the nitric acid of the saltpetre is obtained by simple subtraction. Since ferrous oxide is oxidised by nitric acid according to the equation:

$$6FeO + N_2O_5 = 3Fe_2O_3 + 2NO$$

six molecules of ferrous oxide correspond to one molecule of nitric acid; hence from the amount of oxidised ferrous oxide found may be reckoned the amount of nitric acid required for its oxidation, or what is the same thing, the amount of saltpetre contained in the sample. Seeing, however, that Chili or soda saltpetre would be equally affected by this test, the test only holds good for ascertaining the amount of both nitrates.

Gay-Lussac's Test.—In this test a weighed quantity of saltpetre is mixed with 4 parts of sodium chloride and ¼ part of powdered wood charcoal, and the whole heated to redness. The potassium nitrate and sodium nitrate are thereby converted into carbonates, and the amount of the latter determined by an alkalimetrical process. This test, like the above, gives the total quantity of nitrates present.

Uses.—Saltpetre proper or potassium nitrate is chiefly used in the manufacture of gunpowder. Of late Chili saltpetre has chiefly been used for preparing nitric acid and English sulphuric acid, on account of its cheapness. Saltpetre is used as an oxidising agent as well as a flux in metallurgical operations. For this purpose a mixture of cream of tartar and saltpetre is often employed; when this mixture is heated, the cream of tartar is oxidised at the expense of the saltpetre. When the

mixture consists of 2 parts cream of tartar and 1 part saltpetre, a residue is obtained, consisting of potassium carbonate and an excess of carbon, and is called black flux. When an excess of saltpetre is employed, a residue is left, which is known as white flux; it consists of a mixture of potassium carbonate with undecomposed saltpetre. For most purposes, in the place of black flux, a mixture of potash and soda may be used, and in the place of white flux a mixture of potash and a little saltpetre. Fulminating powder is an intimate mixture of 3 parts saltpetre, 2 parts dry potassium carbonate, and 1 part sulphur; when heated, it first of all melts, then explodes with a violent report. Quick flux consists of a mixture of 3 parts saltpetre, 1 part sulphur, and 1 part sawdust. Bücher's mixture for extinguishing fires consists of 60 to 66 parts of saltpetre, 36 to 30 parts of sulphur, and $3\frac{1}{2}$ to 4 parts of charcoal. Its effect in extinguishing fires depends upon the sudden evolution of a large quantity of sulphurous oxide, which suffocates the flames. Saltpetre is further used in pyrotechnics for preparing different coloured fires, etc.

GUNPOWDER AND OTHER EXPLOSIVE MATERIALS.

History.—The discovery of gunpowder was probably made in India long before our historic era. The Chinese, who were acquainted with the substance in the earliest times, according to most historians, obtained their knowledge of its preparation from the Hindoos. It is, however, curious that neither in India nor China was gunpowder used for throwing projectiles, but only for fireworks. Whether the Chinese at a later period possessed arms suited for gunpowder is uncertain. According to Uffano, an Italian writer, as well as others, arms of the kind were found in some parts of the Chinese coast, in the first century after Christ; but this is disputed by other writers. The art of preparing gunpowder is said to have been conveyed to Europe by the Saracens.

In what relation the art of preparing gunpowder stands to the Greek fire discovered by the Saracens in the seventh century, and employed by them in the conquest of Constantinople, is uncertain. According to some, the discovery of gunpowder was a result of attempts to perfect the Greek fire, and they of course deny that the knowledge of gunpowder was derived from Eastern Asia. According to others there is no relation between Greek fire and gunpowder. The first clear directions for the preparation of gunpowder dates from the eighth century, when Marcus Græcus prepared it by mixing together 1 part sulphur, 2 parts charcoal, and 6 parts saltpetre. After him Albertus Magnus and Roger Bacon, in the thirteenth century, both give similar directions for the preparation of gunpowder; they were probably both of them acquainted with the writings of Marcus Græcus. It is, at any rate, certain that Berthold Schwartz was not the discoverer of gunpowder; for long prior to his pretended discovery, methods were known according to which gunpowder could be prepared, and it is most probable that he prepared his gunpowder according to the directions given by Marcus Græcus.

The common opinion is that gunpowder was first used in Europe at the battle of Crécy in 1346; according to other accounts arms fired by gunpowder existed in England as early as 1327. Whether the Arabs used gunpowder for purposes of war in the thirteenth century in Spain, as some historians declare, is uncertain. The first account of the use of gunpowder in Germany dates from the year 1360, in which year the town hall in Lübeck was burnt down owing to the carelessness of certain gunpowder manufacturers. Gunpowder was, however, known in Germany in 1354.

Composition.—Gunpowder is approximately a mixture of 2 equivalents of saltpetre, 1 equivalent of sulphur, and 3 equivalents of charcoal, and corresponds to the following percentage composition:

Saltpetre	202	74·8
Sulphur	32	11·8
Charcoal	36	13·4

The explosive effect of this mixture upon ignition depends upon the very sudden and almost instantaneous development of permanent and difficultly condensible gases. The chemical change which takes place may be represented by the equation:

$$2KNO_3 + S + 3C = K_2S + N_2 + 3CO_2.$$

Besides this chief process, a number of minor reactions take place when gunpowder is exploded, giving rise to the formation of a number of other compounds; thus, for instance, nearly all the potassium sulphide is oxidised to sulphate. Moreover, the composition of gunpowder is not exactly that given in the above equation, apart from the fact that the charcoal used in preparing gunpowder is not pure carbon, but contains, besides carbon, hydrogen, oxygen, and ash constituents.

The following tables give the results Weltzien obtained, by the analysis of different kinds of gunpowder:

Cannon Powder.

	Baden	Prussian	Bavarian	French
Saltpetre	72·94	75·58	72·50	73·74
Sulphur	12·01	12·45	12·62	13·60
Charcoal — Carbon	10·65	10·12	11·73	10·29
Charcoal — Hydrogen	0·49	0·83	0·73	3·58
Charcoal — Oxygen	1·66	1·33	1·35	—
Water	2·25	1·89	1·61	2·28

Sporting Powder.

	English	German
Saltpetre	79·36	76·95
Sulphur	10·63	11·52
Charcoal — Carbon	8·76	9·58
Charcoal — Hydrogen	0·60	0·48
Charcoal — Oxygen	—	—
Water	0·90	3·60

Blasting powder varies very considerably in composition, as shown by the following table:

	I.	II.	III.	IV.	V.	VI.
Saltpetre	66·36	63·87	68·83	65·5	61·96	70·08
Sulphur	20·95	16·24	15·83	15·0	17·96	11·98
Charcoal	11·75	18·52	15·83	19·5	20·08	18·01
Water	0·93	1·35	—	—	—	—

I. is blasting powder from Mansfeld, analysed by Streng; II. from the Upper Harz; III. from Westphalia; IV. and V. is French blasting powder, and VI. is Italian blasting powder.

According to the researches of Bunsen and Schischkoff, the process of combustion upon exploding gunpowder is very complicated, for not only are nitrogen and carbonic acid produced, but also considerable quantities of carbonic oxide and small quantities of other gases. Besides potassium sulphide, a large number of other solid products are also formed, as shown by the following table:

The composition of the sporting powder employed in the researches was as follows:

Saltpetre	78·99	
Sulphur	9·84	
Charcoal — Carbon	7·69	11·17
Charcoal — Hydrogen	0·41	
Charcoal — Oxygen	3·07	
Water	traces	

One gram of this powder yielded upon explosion the following products:

	Gram
Potassium sulphate	0·422
„ carbonate	0·126
„ hyposulphite	0·032
„ sulphide	0·021
„ sulphocyanide	0·003
„ nitrate	0·037
Carbon	0·007
Sulphur	0·001
Ammonium sesquicarbonate	0·028
Total solid residue	0·680

	Gram		C.C.
Nitrogen	0·099	=	79·40
Carbonic acid	0·201	=	101·71
,, oxide	0·009	=	7·49
Hydrogen	0·0002	=	2·34
Sulphuretted hydrogen	0·0018	=	1·16
Oxygen	0·0014	=	1·00
Total gaseous products	0·314	=	193·10

According to Fedorow's researches, the products of combustion are influenced by the pressure under which they are formed. The higher the pressure, the greater is the proportion of potassium sulphide and carbonate in the residue, and the smaller is the proportion of undecomposed powder. According to the same researches, the reactions ensuing upon exploding gunpowder may be assumed to take place in the following stages. The decomposing saltpetre first ignites the sulphur, and forms potassium sulphate; the excess of oxygen combines with a portion of the carbon, forming carbonic acid, according to the equation:

$$2KNO_3 + S + C = K_2SO_4 + N_2 + CO_2.$$

Nitrogen and carbonic acid are liberated as gases, while the excess of carbon converts the potassium sulphate into hyposulphite and carbonate:

$$2K_2SO_4 + 2C = K_2S_2O_3 + K_2CO_3 + CO_2.$$

When the combustion takes place under pressure, the carbon exercises a further reducing action, forming potassium sulphide:

$$2K_2S_2O_3 + 3C = 2K_2S + 2S + 3CO_2.$$

Finally it is possible for the sulphur to react upon the potassium carbonate according to the equation:

$$4K_2CO_3 + 4S = K_2SO_4 + 3K_2S + 4CO_2.$$

Characters.—*Inflammability of Gunpowder.*—The readiness with which gunpowder takes fire depends upon its composition, upon the size of the grains, the density and relative moisture. The larger-grained gunpowder is the most difficult to ignite. According to Violette, the following kinds of gunpowder require for their ignition the following temperatures:

	Temperature of Ignition
Blasting powder	270°
Rifle powder	276°
Fine sporting powder	280°
Superfine sporting powder	320°

The dust of powder of the same kind takes fire more readily than the corresponding powder itself.

Gunpowder is most easily ignited by bringing it into contact with red-hot substances; less easily by means of a direct flame. Thus, for instance, a jet of ignited illuminating gas requires to be left some time in contact with gunpowder before it takes fire. Gunpowder may, however, be exploded by strong friction or percussion, especially when compressed between metal surfaces. Slaking lime is said to be capable of igniting gunpowder.

Rapidity of Combustion of Gunpowder.—The rapidity with which gunpowder burns is dependent upon the composition and upon the mechanical condition, especially the density. The less dense varieties of gunpowder burn quickest. Highly compressed gunpowder burns very slowly, especially when very fine grained, or when it is mixed with a fine powder. For this reason powder ought never to be rammed very tight into guns.

Three different kinds of density are distinguished in gunpowder:

I. *Mass Density, or Gravimetric Density*, which signifies the relative weight of equal volumes of grain powder. The weight of 1 litre of powder generally varies between 0·820 and 0·203 kilos.

II. *Grain Density*, which signifies the relative density of the individual grains. This varies between 1·4 and 1·9, and is of course greater the more highly the gunpowder is compressed in its manufacture.

III. *Absolute Specific Gravity*, which signifies the specific gravity of the solid mass of the powder, exclusive of the air enclosed between the individual grains. It amounts on the average to 2·0.

The following are the essential characters that good gunpowder should possess:

1. It should have a slate-grey colour. A black colour indicates moisture, bluish black too much charcoal.

2. It ought not to glisten strongly. Light specks indicate saltpetre that has become separated.

3. The grains ought not to be very friable when rubbed between the fingers, and they ought to crackle when crushed. They should not, however, be too hard, since powder that is highly compressed burns too slowly.

4. The grains ought to be, as near as possible, of equal size.

5. Should sharp particles be felt upon crushing a sample of gunpowder between the fingers, it indicates that the sulphur has not been sufficiently finely divided.

6. Upon placing a few grains of gunpowder upon a piece of white note paper, and moving them about by shaking the paper, no coloration of the paper should take place, as this would indicate the presence of moisture or powder dust.

7. A small quantity of gunpowder when burnt upon a piece of paper must burn without leaving any residue, and without igniting the paper; otherwise it is moist, or the carbon particles are not sufficiently finely divided. Yellow streaks indicate an imperfect distribution of sulphur. When the mixing has been imperfect, some grains remain unburnt.

8. Gunpowder when burnt should not evolve a large quantity of poisonous gas, especially carbonic oxide. This requirement is especially necessary in the case of blasting powder, since workmen are often much exposed to the gaseous products of combustion.

Preparation.—The preparation of gunpowder consists essentially of a sequence of mechanical operations, by which the materials are first of all brought, either singly or together, into the state of a fine powder, then intimately mixed together, and the mixture thus obtained is finally condensed, granulated, polished, and dried. The raw materials used in the manufacture of gunpowder must have a certain definite chemical and physical constitution. The essential properties required of them are as follows:

Saltpetre.—Refined saltpetre only can be used; it must above all things be free from chlorine compounds and from sodium nitrate, since these compounds would render the gunpowder moist. The refining of crude saltpetre (*vide* p. 215) for purposes of gunpowder manufacture is carried out either at the powder mills or in special saltpetre refineries. The saltpetre used must always be so pure that a small quantity of it dissolved in water is not rendered perceptibly cloudy when treated with a solution of silver nitrate.

Sulphur.—Of the different kinds of sulphur found in the market, roll sulphur alone is used in the preparation of gunpowder. When sufficiently pure it is at once used for making gunpowder; should it, however, contain mechanical impurities, these must first be got rid of by re-melting: the sand, clay, lime, etc. sink to the bottom of the melted mass, and the pure sulphur can be drawn off. It is then made to cool slowly, so as to render it highly crystalline and brittle, in which state it can be powdered more readily. Flowers of sulphur is not suitable for the preparation of gunpowder, on account of the sulphurous and sulphuric acid it contains. Milk of sulphur is equally unsuitable, because it leaves a fixed residue when burnt.

Charcoal.—The quality of gunpowder is considerably affected by the sort of charcoal used in its manufacture. The charcoal should be light, porous, and easily inflammable; when burnt, it should not give any sensible quantity of ash. A thoroughly burnt charcoal should always be used, because charcoal imperfectly burnt contains so much oxygen that its combustibility is considerably lessened. Charcoal that has been imperfectly burnt is known as red charcoal. Since light kinds of wood yield light charcoal, only light and soft varieties of wood are used in making charcoal intended for the manufacture of gunpowder. In this country the lime, the willow, poplar, horse-chestnut, vine, hazel, cherry, alder, and other kinds of light wood are used for the purpose. In Germany, the wood of the black alder is extensively used. In Italy, where the material is cheap, excellent charcoal for gunpowder is prepared from hemp stalks previously deprived of bast.

According to De Saussure's researches, the trunk wood of the oak contains less ash than any other part of the tree. Trunk wood being taken as unity, he gives the following proportion of ash in the different parts of the oak:

Trunk wood	1
Branches deprived of bark	29
Bark itself	30
Bast	36
Leaves	36

Hence it is obvious that, as charcoal for making gunpowder must be as free as possible from ash, it is a matter of no slight importance which part of the tree the wood is taken from. The only parts fit for this purpose are the trunk and thicker branches of trees five to six years old.

The season of felling timber has great influence upon the amount of ash in wood. The most suitable season is spring, because at this period, although the wood is full of sap, the sap is very much diluted with water, and it contains but very small quantities of solid saline constituents. Wood for making charcoal intended for the manufacture of gunpowder ought therefore to be felled in spring, or at latest in the early part of September.

Preparation of Charcoal for making Gunpowder.—The manner in which the charcoal is prepared affects its characters, and the relative amount obtained, very considerably. The lower the temperature at which the charcoal has been prepared, the more inflammable it is; but at the same time it is more hygroscopic, and contains less carbon and more oxygen. The relative amount of charcoal obtained is also greater the lower the temperature of carbonisation. Violette gives the following estimate of the relative amount of charcoal obtained from dry wood at different temperatures:

Temperature	Percentage of Charcoal
250°	50
300°	33
400°	20
1500°	15

The lowest temperature at which wood can be carbonised is 250°.

An essential necessity in preparing good charcoal for making gunpowder is that the wood should be dry. The wood before being carbonised is stored up six or nine years in well-ventilated chambers. It was formerly customary before drying the wood, to expose it several years to the action of rain, so as to wash out the sap; and thus wood was obtained containing less ash constituents. The same object is now effected by treating the wood with superheated steam.

Carbonisation in heaps is not adopted in preparing charcoal for gunpowder manufacture, because the carbonisation is unequal, and the charcoal is also mixed with clay, sand, etc., materials used in covering the heaps. For the same reason the carbonisation in pits is also unsuitable.

Carbonisation in Pits.—This method is still in use in some parts of France. Pits about four feet deep and four feet wide are dug in the earth and filled with the wood to be carbonised, a first small portion being introduced alight so as to commence the process of carbonisation. During the entire operation the pit is covered with a metal lid to keep out the air, which would otherwise cause the combustion of the top layers of charcoal, the lid being provided with small holes for the escape of the gases evolved. The yield is about 23 per cent. of charcoal, which however, is not quite uniformly carbonised, the charcoal lying against the comparatively cooler sides of the pit being less strongly carbonised than that in the interior.

Carbonisation of Wood in Cylinders.—This is the most general method of preparing charcoal intended for the manufacture of gunpowder. In the Prussian powder works the cylinders are of cast iron, and are about 6½ feet long and 2 feet wide; both ends admit of being closed with a cast-iron lid. The front lid is furnished with a small opening, admitting of being closed, for taking out tests; the hinder lid is furnished with a tube for taking off the gaseous products of carbonisation, which are passed through a number of condensing tubes where the tar is deposited, and the more volatile portion is passed into a kind of tower, after which it escapes into the air.

In some places, the products of carbonisation are passed into the fire and burnt. It is in any case necessary to let these products escape freely, without being exposed to pressure in the condensing and purifying apparatus, because it has been found that otherwise the charcoal easily becomes covered with a slimy soot, which retards its combustion.

The fire is so arranged that the flame plays round the cylinder on all sides. In order to prevent the lower part of the cylinder from being heated more than the other parts, it is coated at the bottom with fire clay. As a rule, a couple of cylinders are placed over each fire, and wood is used as fuel.

A cylinder of the dimensions above given admits of being charged with 2 cwts. of black alder wood. The wood is cut into billets about a foot long, and laid in the cylinder in such a way as to leave only a very small air space. The cylinders are first heated strongly for 3 or 4 hours, the temperature being afterwards somewhat reduced, and the process of carbonisation is complete in about 12 hours. The charcoal is then allowed to cool, and placed in air-tight sheet-iron vessels, where the cooling process

is completed. The amount of charcoal obtained by this process is about 20 to 30 per cent. The amount obtained in the powder manufactory at Dresden is about 27·4 per cent., while in France a precisely similar process yields on the average 34 to 35 per cent. The amount of charcoal may, of course, be increased or lessened according to the duration and the degree of the heating.

Carbonisation by Superheated Steam.—Violette has constructed an apparatus of this kind by which excellent charcoal is obtained for gunpowder manufacture. It consists of an iron cylinder, one end of which is closed and the other open. This cylinder is fitted inside a wider cylinder closed at both ends in such a way that a space is left between the two cylinders. Beneath the cylinders is a fire, the hot air from which first plays round a spiral wrought-iron steam tube, and then upon the outer cylinder. Steam is passed from a boiler through the serpentine tube into the space between the two cylinders. The charging of the inner cylinder with wood is effected by removing a lid in the front of the outer cylinder, and pushing in the wood packed in a perforated cylinder; the lid is then closed and luted. An iron tube conveys the products of carbonisation from the inner cylinder direct into the air.

The tension of the steam is not more than 1 atmosphere. The time required for carbonisation is only one and a half to two hours; the charge is each time 50 to 70 lbs. of wood. The emptying of the apparatus is effected by removing the lid of the outer cylinder, and drawing out the perforated cylinder containing the charcoal into a suitable close vessel, where it is allowed to cool. The cylinders are then immediately recharged.

The following table gives the results of analyses, by Kahl, of charcoal prepared in the Dresden powder factory:

	By simple Carbonisation	By Carbonisation with Superheated Steam		
		At 350°	At a higher temperature	
Carbon . . .	87·9	75·0	79·6	85·0
Hydrogen . . .	2·6	4·1	3·8	3·3
Oxygen . . .	7·8	19·5	15·0	10·1
Ash	1·6	1·4	1·6	1·6

The red charcoal prepared by Violette at a low temperature contains on the average only about 70 per cent. of carbon.

According to the old method of making gunpowder, the pulverisation, mixing, and condensation are carried out in a single operation. For this purpose the charcoal or the charcoal and sulphur are powdered in a moist state, by a stamping machine, and then the saltpetre is added, in a fine state of division. This operation can be equally well performed by mill stones. But since it is difficult to effect a perfect pulverisation of a moist mass, it is now usual to pulverise the three ingredients separately, then to mix and compress them.

The PULVERISATION is performed either by stampers, mill stones, or revolving drums.

Pulverisation in Stampers.—The stampers are made of wood, the weight of each being about 1 cwt. The stampers are fitted with a bronze shoe, and are alternately lifted, by means of a wheel furnished with teeth, and allowed to fall into a bed. The beds containing the material to be reduced to powder are arranged in numbers corresponding to the stampers, and set in a block of very hard wood.

Grinding by Mill stones.—Two heavy vertical runners of stone or cast iron, similar to those used for crushing linseed, revolve round a vertical axis on a fixed horizontal bed. The material to be powdered is spread upon the bed and is crushed by the runners. The mass is stirred, and brought equally under the revolving stones by means of scrapers fixed behind each runner.

Pulverisation by Revolving Drums.—This method came into use during the French revolution, and consists in placing the substance to be pulverised, together with a number of bronze balls, in a wooden drum turning upon a horizontal axis, and then rotating the drum. The drums are furnished internally with wooden ledges running in the direction of the axis of the drum, and covered with leather. The materials are placed in the drum through a little door at the periphery of the drum, and upon setting the drums in motion are quickly reduced to powder. When the materials have been sufficiently powdered, the drum is turned so that the door is downwards, and on

opening it the powder falls out into a vessel placed beneath. The bronze balls are prevented from falling out by a sieve attached to the opening.

Mixing the materials.—This operation is carried out in drums of precisely the same construction as those above described; they are either made of wood, covered internally with leather, or are made entirely of leather. The bronze balls are smaller, and the sieve for letting out the powder is also proportionately finer than in the pulverising process.

Moistening.—The gunpowder is placed in wooden boxes, and sprinkled at intervals with water, until it has taken up 8 or 10 per cent. The moistening process is sometimes performed in the drums.

Pressing.—The object of this operation is to give coherence to the powder and such consistency that it can be granulated. It requires much care; for if the gunpowder be too highly compressed, it burns too slowly; the heating of the gases is less sudden, their expansive force consequently less. On the other hand, gunpowder that has not been sufficiently compressed burns too quickly, and has an explosive effect. The ordinary method of compressing gunpowder consists in passing the mixture through a rolling mill, consisting of two rollers, the upper one of bronze, and the lower one of wood; by means of a lever arrangement they can be pressed against one another so as to exert a pressure of twenty to twenty-five tons. The mixture is conveyed to the mill, already set in slow motion, by means of an endless cloth, and is pressed between the rollers to a cake of about $\frac{1}{4}$ in. thick. The caking may be also effected by means of hydraulic pressure; for which purpose the mixture is laid upon copper plates, and pushed by jerks under the press. It has been already mentioned that the operation of pulverising the materials by stampers may be combined with the caking or compressing operation. Neimke suggests a method according to which the saltpetre is dissolved in water, and the mixture of charcoal and sulphur added in a fine state of division; the mixture is stirred and heated until about 15 per cent. of water remains. When cool, the mass is pressed between rollers or stampers.

Granulation.—The object of this operation is to reduce the powder cake into grains of a definite size, according to the purpose for which the powder is to be used, the rapidity of the combustion of gunpowder depending upon the size of the grains. Gunpowder dust and caked powder both burn very slowly, while granulated powder, owing to the intermediate hollow spaces between the grains, burns much quicker.

Three or four sieves are generally used in the granulating process, through which the powder is passed. These sieves are made of wood, parchment, or metal; they are round in shape and are placed above one another in such a way that the uppermost sieve has the biggest holes, the holes in the ones beneath gradually decreasing in size; the holes in the last sieve are so fine that powder dust only can pass through them. The sieves are all set in a frame, and the uppermost sieve is covered with a wooden lid. Powder in the form of cake is placed in the uppermost sieve through a funnel and linen tube attached to the lid, and a shaking motion communicated to the sieves, by means of which a rubber of hard wood is set in motion and breaks up the powder cake into pieces which are separated in succession by the sieves. The grains which are too large to pass through the second sieve are carried off through an opening at its side, and are again exposed to the action of the rubber in the first sieve. The same plan is followed out in the third and fourth sieve, with the exception that the grains which do not pass through the last sieve are not again put into the upper sieve, but are separately collected. The uppermost sieve is termed the first sieve, the lowest sieve the dust sieve, and the intermediate ones the corning sieves. By this means different grained varieties of powder are obtained, and the dust passing through the last sieve is separately collected. In Lefevre's corning machines eight or twelve such sieves are fitted in boxes hung upon a beam, and they are set in motion by a special mechanical contrivance.

Congreve's Granulating Process.—The powder cake is first of all forced through a shot sieve and the broken mass granulated by passing it between three pairs of rollers furnished with pyramidal teeth. The teeth of the first pair of rollers are larger than those of the second, and the latter larger than those of the third pair. The teeth are set so near one another that they are almost in contact. The powder cake is brought into the rollers by means of an endless cloth. Beneath each pair of rollers passes an endless sieve, upon which the powder falls, and the sufficiently fine grains pass through the sieve, while the coarser mass is conveyed to the next pair of rollers. At the lowest part of the granulating apparatus, a couple of endless sieves of unequal fineness pass over one another to catch the powder passed through both the upper sieves and the lowest pair of rollers, separating it into coarse and fine grained powder and powder dust.

Champy's Method.—According to Champy's method the powder is granulated in revolving drums, by injecting water in a fine stream from the axis of the drum. Each drop of water upon falling upon the powder forms with it a small adhesive lump, which is increased in size by the movement of the drum. The drums are made to revolve until the grains have attained the required size. The mass is then taken out and sorted through sieves, the grains that are too large being powdered again, and replaced with the powder dust in the drums.

The granulated powder is then superficially dried upon pieces of cloth stretched upon frames, the frames being placed in the drying house upon wooden supports and exposed to a current of air.

Polishing of Gunpowder.—This operation is not carried out in all countries with every kind of powder, since powder thus treated does not so readily take fire as unpolished powder. On the other hand, polished powder has the advantage that it does not so readily absorb moisture, nor does it so readily discolour substances brought in contact with it, and it is less friable. For polishing gunpowder, granulated powder is brought into horizontally placed drums with a smooth internal surface, and the drums are caused to rotate slowly for a few hours. The addition of graphite, so as to give the powder grains a more shiny appearance, is not to be recommended, on account of its rendering the powder less readily inflammable.

Instead of simple drums, in some manufactories rolling tubs are employed, which are divided lengthways into several compartments, each compartment being furnished with a special door for admitting the powder to be polished.

Drying of Gunpowder.—Before gunpowder is dried it may be conveniently pressed into pieces having the shape of cartridges. This operation may be effected by the aid of a gentle heat without it being necessary to surround the powder with cases of paper or metal. The so-called prismatic powder consists of six-sided columns of this kind perforated lengthways with seven holes.

Gunpowder requires drying very carefully, a very slight and gradual heating being necessary at first; for if this is neglected the grains are liable to crack, and an efflorescence of saltpetre is apt to take place. The powder is either dried in the air or in chambers artificially heated.

Drying in the Air.—The powder is spread in layers $\frac{1}{2}$ to $\frac{1}{4}$ inch thick upon tables covered with cloth, the mass being often turned until dry. In some places the drying is assisted by allowing the rays of the sun to fall upon the powder, while in others the sun is kept off by roofing-in the drying chamber. In the former case the powder dries in about four hours, in the latter in about ten hours. Where the ground is moist the floor must be covered with asphalte, to keep the moisture from the powder.

Drying in artificially heated Chambers.—The powder is spread out upon hurdles supported upon wooden frames fastened in the sides of the chambers, which are generally heated up to 40°–50°. An oven is placed in the middle of the chamber. In large powder works the powder is dried by steam, for which purpose it is spread out on pieces of linen stretched on frames, which lie above one another, the steam pipes passing under the frames. Gunpowder is also sometimes dried by placing it in drying boxes, and passing air previously heated in iron tubes into the boxes. In all cases care is taken to avoid heating the drying chambers above 60°.

Removing the Dust.—For this purpose the powder is passed through linen tubes having a sloping position and kept in constant agitation; the powder dust escapes through the meshes of the linen, while the powder grains fall out at the lower extremities of the tubes and are collected for use.

Gunpowders of Different Composition.—Attempts have long been made, by partial or entire replacement of the ordinary constituents of gunpowder by other substances, to alter its composition so as to render it less dangerous, and at the same time to increase its energy and render it cheaper.

Thus, for instance, attempts have been made to replace the saltpetre either entirely or in part by potassium chlorate. It was however found that a powder thus prepared was very liable to cause accidents, owing to its taking fire when struck, and further that, from its developing when ignited too suddenly large volumes of gases, fire arms burst, and were moreover much corroded by the action of free chlorine. Some value may be however attached to Augendre's white powder, which, according to Pohl, has the following percentage composition:—

Potassium chlorate	49
Cane sugar	23
Potassium ferrocyanide	28

This powder is not easily ignited by a blow, but very easily by contact with flame

or a red-hot body. It is said to be more effective than gunpowder, 60 parts of white powder yielding the same volume of gas as 100 parts of ordinary gunpowder. It leaves when burnt only a very small residue; it has a low temperature of ignition, and does not readily absorb moisture. On the other hand, it is far more easily ignited by a blow than gunpowder; it attacks the barrels of fire arms, and is dearer than gunpowder.

A great number of attempts have been made to replace saltpetre by Chili saltpetre, which is much cheaper. The disadvantages, however, are that, when the latter is not perfectly pure, a very hygroscopic gunpowder is obtained, and even when the salt is pure the gunpowder made from it burns too slowly.

Wagner proposed using barium nitrate as a substitute for potassium nitrate. A powder thus prepared, known as saxafragin, is certainly less inflammable than gunpowder; but it is, on the other hand, specifically heavier, and leaves when burnt a considerable residue. According to Wynand, saxafragin has the following percentage composition:—

Charcoal	22·0
Barium nitrate	76·0
Saltpetre	2·0

Nobel's Blasting Powder.—This is a powder containing nitro-glycerine, and is composed as follows:—

	I.	II.
Charcoal	12	10
Barium nitrate	68	70
Nitro-glycerine	20	20

Still greater in number are the substitutes proposed for charcoal, the chief of which are tannic acid, tan, sawdust, flour, starch, sugar, potassium ferrocyanide, cream of tartar, etc. Ehrhardt's blasting powder consists of—

Saltpetre	12·25
Charcoal	49·00
Tannic acid	24·50
Potassium chlorate	14·25

In the above powder the sulphur itself is replaced, which is seldom the case.

Schultze's gunpowder consists of granulated nitrified wood, impregnated with potassium nitrate; 100 parts of nitrified wood are brought into a solution consisting of 26 parts potassium nitrate and 220 parts water, and eventually dried at a temperature of 32° to 44°. The saltpetre may be replaced in part by barium nitrate.

Tests for Gunpowder.—The effect of gunpowder depends upon its forming when ignited hot gases, which occupy a very considerably larger volume than the powder itself. Gunpowder is consequently the more effective the larger the volume of gases evolved, and the higher the temperature produced by its combustion, for the volume of a gas or mixture of gases increases, and the force of expansion is greater, the higher the temperature under which it is formed. However, the evolution of gas when gunpowder is burnt must not be too sudden, for in such case the ball would not have time to leave the barrel before the force of expansion would be conveyed to the sides of the barrel and burst the gun. On the other hand, the combustion must not be too slow, as in such case the ball would leave the barrel before the combustion is complete, and a part of the gases developed by the combustion would be without effect upon the ball.

According to Bunsen and Schischkoff, the temperature produced by burning gunpowder in a closed space is 3340° C. The volume of the gases produced, reduced to 0°, exceeds the volume of the solid powder 193·1 times. Accordingly at the temperature of combustion (3340°), the volume of gases is 2369 times that of the solid powder.

Testing the effect of Gunpowder.—A number of methods have been given for testing the effect of gunpowder, which depend chiefly upon ascertaining either the distance a ball is projected, the height to which a weight is lifted, or the pressure exerted upon a lever by a known quantity of gunpowder.

Mortar Test.—For this purpose a given weight of the powder is placed in a bronze mortar furnished with a powder chamber just large enough to hold that quantity. A heavy bronze ball of known weight is then placed upon the powder, the mortar inclined to an angle of 45°, and the powder fired. The quality of the powder is indicated by the distance to which the ball is projected.

Rod Test.—This test, which is chiefly in use in Austria, is performed as follows. A known quantity of powder is placed in a small mortar, into the mouth of which fits

accurately a weight of 5 lbs. The weight is moveable between a couple of vertically placed rods, one of which is furnished with teeth, and a ratchet work prevents the weight from falling back, retaining it therefore at the height it is projected by the powder.

Lever Test.—For this test a jointed lever is employed, to the one arm of which a small mortar is attached in such a way that in burning a small quantity of powder (2 ounces) the force of reaction causes it to turn a certain distance, so that the other arm of the lever to which a weight is attached is raised proportionately. A small ratchet, which is pushed, during the turning, along a toothed sector, prevents the lever falling back into its former position; so that, after the explosion of the powder, the height to which the weight has been raised may be read off.

Regnier's Powder Test.—A double-limbed steel spring, mounted so as to move freely, is set with the one limb connected with the mouth, the other limb with the button of a small cannon; so that upon firing the powder both limbs—the one being propelled forwards by the powder, the other in a contrary direction by the rebounding of the cannon—approach one another. The extent to which they approach one another gives a measurement of the force exerted by the powder.

Pistol Test.—A graduated wheel, supported by a spring, executes a revolution corresponding to the force of the powder. The rotatory motion is given to the wheel by an arm attached to it, which terminates just before the nozzle of a pistol.

GUNCOTTON.

History.—The substance known as guncotton, or pyroxilin, was discovered in 1846 simultaneously by Schönbein, by Boettger, and by Otto. It caused a great deal of excitement at that time in scientific as well as in political circles, since it was supposed to be a destructive agent of extraordinary power. It has, however, been since ascertained that the essential feature of this discovery consisted in better methods of preparing and applying materials that had been long known. In 1833 Braconnot had prepared an easily inflammable substance which he termed xyloidin, from the same materials which are now employed in the preparation of guncotton. In 1838 Pelouze gave this substance his attention, and found that it might be exploded by concussion; shortly afterwards Dumas prepared the same substance, and called it nitramidin.

Composition.—Guncotton consists of cellulose, in which part of the hydrogen is replaced by NO_2; it is obtained by treating any kind of cellulose with very concentrated nitric acid. The nitric acid is decomposed, and for every molecule of decomposed nitric acid, one atom of hydrogen in the cellulose is replaced by the group NO_2. The number of hydrogen atoms replaced in a molecule of cellulose is dependent upon the concentration of the nitric acid employed. Consequently guncotton must not be considered as a substance of constant composition, but on the contrary there are a number of different kinds of nitro-cellulose, and guncotton consists either of one of these nitro-compounds or of a mixture of several. It is only in this way that we can explain the difference in composition between samples of guncotton prepared in different ways.

This may be best understood by considering cellulose as a polyacid alcohol, *i.e.* as a sex-acid alcohol derived from the water type.

Water Type $\left.\begin{matrix}H_6\\H_6\end{matrix}\right\}O_6$ Cellulose $\left.\begin{matrix}C_{12}H_{14}O_4\\H_6\end{matrix}\right\}O_6$

We have therefore in cellulose six typical atoms of hydrogen, which are capable of being replaced by NO_2.

Accordingly, by acting upon the molecule of cellulose with one molecule of nitric acid, mononitro-cellulose is produced:

$$\underset{\text{Cellulose}}{\left.\begin{matrix}C_{12}H_{14}O_4\\H_6\end{matrix}\right\}O_6} + \underset{\text{Nitric Acid}}{\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O} = \underset{\text{Mononitro-cellulose}}{\left.\begin{matrix}C_{12}H_{14}O_4\\NO_2H_5\end{matrix}\right\}O_6} + \underset{\text{Water}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}$$

By the action of two molecules of nitric acid:

$$\left.\begin{matrix}C_{12}H_{14}O_4\\H_6\end{matrix}\right\}O_6 + 2\left(\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O\right) = \underset{\text{Dinitro-cellulose}}{\left.\begin{matrix}C_{12}H_{14}O_4\\2(NO_2)H_4\end{matrix}\right\}O_6} + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

By the action of three molecules of nitric acid:

$$\underset{\text{Trinitro-cellulose}}{C_{12}H_{14}O_4\{H_6\}O_6} + 3\left(\frac{NO_2}{H}\right\}O) = \underset{\text{Trinitro-cellulose}}{C_{12}H_{14}O_4\{3(NO_2)H_3\}O_6} + 3\left(\frac{H}{H}\right\}O).$$

These compounds have therefore a composition analogous to the compound ethers, as is shown by their chemical characters. Thus, for instance, when heated with potassium hydrate, they react like compound ethers. Ethyl nitrate, for instance, when boiled with potash, is converted into ethyl alcohol and potassium nitrate:

$$\underset{\text{Ethyl Nitrate}}{\frac{C_2H_5}{NO_2}\}O} + \underset{\text{Potash}}{\frac{K}{H}\}O} = \underset{\text{Ethyl Alcohol}}{\frac{C_2H_5}{H}\}O} + \underset{\text{Pot. Nitrate}}{\frac{K}{NO_2}\}O}$$

Trinitro-cellulose, treated in like manner, is converted into cellulose and potassium nitrate:

$$\underset{\text{Trinitro-cellulose}}{C_{12}H_{14}O_4\{3(NO_2)H_3\}O_6} + 3\underset{\text{Potash}}{\left(\frac{K}{H}\right\}O)} = \underset{\text{Cellulose}}{C_{12}H_{14}O_4\{H_6\}O_6} + 3\underset{\text{Pot. Nitrate}}{\left(\frac{K}{NO_2}\right\}O)}$$

With reducing agents such as alkaline solutions of hydrogen sulphide, ferrous chloride, mercury and sulphuric acid, etc., guncotton reacts like the nitrates, cellulose is reproduced, and the nitric acid is completely destroyed. This is a proof that in these compounds the radical NO_2 takes the place of the typical hydrogen, and does not, as some suppose, replace hydrogen in the radical; for in such case a nitrogenous compound would be produced by reducing agents in the same way that aniline is obtained by treating nitrobenzyl with an alkaline solution of sulphuretted hydrogen, or with ferrous chloride.

Characters.—Guncotton dried at the ordinary temperature ignites when heated to 175°–185°, while guncotton which has been dried by the aid of artificial heat is far more readily ignitable, exploding at the temperature of boiling water; indeed in many cases it has been found that guncotton thus prepared explodes without any apparent cause. The products of combustion obtained when guncotton is burnt differ in quantity and composition according to the difference in composition of the guncotton. Thus one observer obtained from 1 gram of guncotton 483 cc. of gas (reduced to a temperature of 0°), while another obtained from the same quantity of guncotton 588 cc. of gas. The gaseous products of combustion consist of nitrogen, nitric oxide, cyanogen, carbonic dioxide, carbonic oxide, and steam. The explosive force of guncotton in fire arms is from two to six times greater than that of an equal weight of gunpowder. Guncotton, when properly prepared, care being taken to use pure acid and pure cotton, leaves no residue when exploded, nor is any acid formed. In these respects guncotton has an advantage over gunpowder; but it has the disadvantage that, owing to the gases produced by the explosion being formed too suddenly, fire arms are subjected to a greater shock.

When kept for a long time, guncotton gradually decomposes. Red vapours are evolved, the mass becomes viscous in consistency, deliquescing eventually to a syrup-like liquid. Active decomposition is sometimes attended with explosion.

Guncotton prepared in the way above described is completely insoluble in alcohol and water, difficultly soluble in ether and solutions of ether in alcohol, and slightly soluble in ethyl acetate. In respect to solubility in ether, alcoholic ether, and ethyl acetate, this kind of guncotton behaves very differently from another kind of guncotton prepared by treating cotton with potassium nitrate and sulphuric acid (*vide* Collodion).

Great precautions are required in the manufacture of guncotton on a large scale.

The first necessity is that the acid mixture should be quite cold before the cotton is added. Besides this, care must be taken that the quantity of acid mixture employed is sufficient to completely cover the cotton; and it is also necessary that the cotton should be covered by the acid mixture as quickly as possible. Should a part of the cotton protrude beyond the surface of the acid liquid, spontaneous heating very quickly takes place, and decomposition sets in, accompanied by the evolution of red vapours. This decomposing action, if not quickly stopped, is apt to cause the ignition and explosion of the whole mass.

Preparation.—For preparing guncotton, a mixture is made of 3 vols. concentrated nitric acid and 7 vols. concentrated sulphuric acid. When cool, a quantity of well-purified cotton is placed in about twenty times its weight of the mixture. After being left to stand for one hour, the guncotton is taken out and pressed between a couple of iron plates, so as to remove the excess of acids; it is then thrown

into water for complete washing. The acids, owing to their high concentration, do not attack the iron plates. The removal of the acids is more easily effected by means of a centrifugal machine, the drum of which retains the guncotton while the acid runs off. The concentrated acid mixture is collected for further use. So soon as the excess of acid has been got rid of, water is brought into the revolving drum, and is driven by the centrifugal force against the guncotton, penetrating its mass and washing out the acid. When the escaping water ceases to taste acid, a dilute solution of soda ($\frac{1}{2}$ per cent.) is passed into the drum to neutralise the last traces of acid, the guncotton is again washed with water, and then finally dried as far as possible in the drum. The final drying is effected by causing a strong current of air to pass over the guncotton at the ordinary temperature, without the aid of artificial heat.

In a carefully conducted operation, the proportion of guncotton obtained from cotton is about 332 parts by weight of guncotton for every 200 parts of cotton employed.

Explosive Paper.—The preparation of this substance is essentially the same as that of guncotton. Special care is however required to avoid tearing the sheets of paper during the treatment with acid, and during the washing process.

Pyroxam, or Explosive Starch.—The starch requires previous drying, which according to Payen is best effected in vacuo at a temperature of 125°. After cooling in a closed vessel, the starch is brought into the acid mixture, the proportion of the latter being equal to 15 times the weight of starch taken. After six hours, the pyroxam is taken out, washed with water, and then dried in a current of air. Payen recommends drying it in vacuo at the ordinary temperature.

All the above substances when prepared in the same manner have the same composition, although, as we have seen, the composition can be very different, affecting the properties of the substance, especially its ignitability. It may be assumed in general that the projectile force of the gases of decomposition is in direct proportion to the temperature required for ignition, so that the greatest amount of projectile force may be expected from a preparation which ignites spontaneously at a temperature of about 180°, while on the other hand the least amount of projectile force would be expected from a compound which ignites spontaneously at 100°. The latter kinds have also the disadvantage that amongst the products of their decomposition there is nitrous acid, which acts most injuriously upon fire arms, and when such compounds are used in blasting, the nitrous acid attacks the lungs of the workmen.

The difference in constitution shown by the different kinds of nitro-cellulose compounds is not only due to the difference in the way of preparing them, but also to differences in the constitution of the raw cellulose material, especially its density and the cohesion among its particles. Cotton in which the individual tubes are thin walled and delicate, and the cohesive force equal throughout, offers at the same time the greatest surface to the action of the acid, and owing to its homogeneity spreads the ignition quickly throughout its mass, and consequently when free from foreign ingredients it yields the best preparations, and such only ought to be used in fire arms. Preparations made from cotton, or linen rags, or paper, are extremely dangerous; owing to the different thickness and different characters of the individual fibres, they ignite at a very low temperature. Preparations of this kind have been the cause of accidents both by spontaneous ignition and the bursting of fire arms, the trajectile force they communicate to the projectile being also slight and uncertain.

Pyroxam is very ignitable, igniting between 90° and 100°; it is also a very unstable product, decomposing at the ordinary temperature, either very quickly with explosion, or gradually with evolution of red vapours and conversion into a syrupy mass; this decomposition is favoured by a moist atmosphere.

The spontaneous decomposition of all the nitro-cellulose compounds is promoted by the presence of a trace of free acid; the washing-out process therefore requires great attention. The action of heat upon these compounds produces a further alteration. Their spontaneous ignition takes place at a lower temperature when they have been kept for some time at a temperature of from 50° to 60°. Thus guncotton, which does not ignite till heated to 180°, will readily take fire at 108°, when it has been heated for twelve hours to a temperature of 50° or 60°.

The difference in ignitability of these bodies may be demonstrated in the following way. Three strong glass tubes are filled respectively with pyroxam, badly washed explosive paper, and good guncotton, and all three tubes heated in a saturated solution of salt. It will then be found that pyroxam is the first to explode; after a short time when the liquid has got hotter the explosive paper ignites, while the guncotton does not ignite even upon boiling the solution of salt.

The point, however, at which guncotton takes fire is considerably lower than that at which gunpowder explodes. This may be demonstrated by spreading a small

quantity of gunpowder upon a sheet of paper, laying upon it a piece of guncotton, and then holding the sheet of paper a short distance over a flame. After a short time, the guncotton suddenly burns away with a flash, while the gunpowder remains unchanged.

Uses.—The application of guncotton in fire arms has shown that its projectile force as compared to gunpowder is as 4 to 1. Cartridges for sporting guns holding 3·2 grams of powder cannot with safety be replaced by guncotton cartridges charged with more than 0·8 gram of the latter. In like manner, military fire arms which require 8·9 grams of powder for propelling a bullet weighing 25 grams, require only 2 grams of guncotton to produce the same effect. It appears, however, that in the larger kinds of fire arms the difference between the effect exerted by gunpowder and guncotton is relatively less.

The difference between the force exerted by guncotton and by gunpowder is not proportionate to the amount of gaseous products developed in their combustion. A kilogram of gunpowder when burnt yields 450 to 500 litres of gaseous products, while an equal weight of guncotton yields 600 to 800 litres of gaseous products (both reduced to a temperature of 0°). The greater projectile force so often observed in the case of guncotton can therefore only be explained by the assumption that the gas formed upon burning guncotton acquires a higher temperature, and consequently greater expansive force, than the gas formed by gunpowder.

Advantages of Guncotton.—Since a given weight of guncotton is more effective than the same quantity of gunpowder, its transport is easier; it is not altered by moisture, or even by soaking in water; it does not soil fire arms like gunpowder; when used in sporting guns the shot is less scattered than is the case when gunpowder is used.

This last fact may be understood by assuming that the complete decomposition of guncotton takes place within a very small space in the gun, in consequence of which the shot receives its entire velocity before leaving the gun. On the other hand the complete explosion of powder requires a longer time, extending over the entire length of the barrel, and even beyond it so as to cause a lateral deviation of some of the shot.

These advantages are somewhat modified by guncotton being dearer than gunpowder; the chief disadvantage however in the use of guncotton is its injurious effect upon the fire arms. These considerations have checked its general application.

The property possessed by guncotton of exploding when struck has led to attempts being made to use it in the place of percussion caps, but at present without any successful result.

The effect exerted by explosive paper is irregular, and is exerted more upon the barrel than upon the projectile. These inconveniences are greater in proportion to the thickness of the paper. For this reason the use of explosive paper is now given up.

The last result attained by the use of guncotton in the place of gunpowder is its application to blasting purposes, where its entire explosive force is brought to account and where the disadvantages are too insignificant to be worth noticing. The general application, however, of guncotton for blasting purposes is retarded by its high price, which at present is not counterbalanced by its greater explosive effect. It may however be expected that, by means of manufactories well arranged and conducted, guncotton will become cheaper, especially as the greater part of the acid employed admits of being turned to further account. The mixture of acids recovered by pressing, and with the centrifugal machine, amounting to about 70 per cent. of the entire quantity, is not strong enough to be used again; but it might either be sold to sulphuric acid manufacturers or the nitric acid distilled off.

The explosive force of guncotton is considerably increased by mixing it with potassium chlorate or potassium nitrate, which is effected by saturating it with solutions of these salts and then drying it.

Testing of Guncotton.—The only possible adulterant capable of being used for adulterating guncotton is ordinary cotton. Both substances are readily distinguishable under the microscope. By moistening a mixture of the kind with solution of iodine, and adding a drop of sulphuric acid, the guncotton assumes a yellow colour, while the cotton becomes blue. Besides this, ordinary cotton is transparent, and is seen to consist of fine tube-like cells, while guncotton presents an entirely altered appearance, the cell character being no longer recognisable.

It has often happened that violent explosions have occurred in magazines and manufactories of guncotton without any apparent cause being traceable, and in rooms that had not been entered for several days. The probable cause of such explosions is the heat developed by gradual decomposition and the increase of surrounding temperature up to the point of ignition, owing to the non-conductive power of the mass. The liability to explosion would of course be increased by the presence of more easily ignitable nitro-substances. Payen refers an explosion that occurred in Vincennes to

this cause. The guncotton there stored up was prepared from hemp, which according to Malagutti contains starch, which would have been converted during the nitrification into the easily ignitable and decomposable pyroxam.

Accidents have also occurred in filling rockets into which the guncotton was driven with great force, and this is not astonishing, since it is a well-known fact that a simple blow suffices to explode guncotton.

NITROGLYCERIN.

During the last few years attempts have been made to replace guncotton by the compound known as nitroglycerin, or Nobel's blasting oil, the explosive properties of which exceed those of guncotton. Nitroglycerin has a composition represented by the formula:

$$\left.\begin{matrix} C_3H_5 \\ 3(NO_2) \end{matrix}\right\} O_3$$

and is accordingly the nitric ether of glycerin. For preparing nitroglycerin, 500 parts by weight of glycerin are slowly poured into a cold mixture consisting of 2200 parts concentrated sulphuric acid and 1100 parts very concentrated nitric acid; the whole is allowed to stand for ten minutes, and then poured into a quantity of cold water equal to six times its volume, taking care to stir the mixture constantly the whole time. Nitroglycerin then separates in the form of a heavy oil, which is freed from acid by repeated washing with cold water. Nitroglycerin has all the explosive properties of guncotton in a greater degree; rapid heating, or a blow, causes its immediate explosion, and these circumstances have led to terrible accidents. A special danger accompanying nitroglycerin consists in its tendency to crystallise at low temperatures; attempts to remelt these crystals too quickly often cause the entire mass to explode.

For blasting purposes a quantity of nitroglycerin is poured into the bore hole, covered up with sand and ignited with a fusee. The effect produced is most astounding.

The material known under the name of dynamite is a preparation of nitroglycerin; it is not so dangerous as nitroglycerin, owing to its only exploding when ignited and not by a simple blow.

SODIUM.

Symbol Na. Atomic Weight 23.

History.—This elementary substance was discovered in 1807 by Sir H. Davy, about the same time as potassium, and the result of the isolation of this metal was to establish the analogy between soda salts and the salts of other metals, which had been long suspected, and was more definitely suggested by Lavoisier in 1787.

Occurrence.—Sodium does not occur naturally in the free state, but in combination with some other elementary substances it occurs very abundantly; as chloride it occurs in the solid form as rock salt, and in a state of solution in sea water and the water of many mineral springs. Sodium also occurs, combined with oxygen and various acid oxides, in the form of salts; thus, for instance, the nitrate occurs abundantly as cubic nitre, the sulphate as thenardite and in the hydrated state as mirabilite; the carbonate occurs as soda and trona, and the borate as tincal or borax. In the oxidised state sodium also enters into the composition of a great number of siliceous minerals, such as albite, labradorite, oligoclase, mesotype, and other zeolites, nephelin, sodalite, achmite, lapis lazuli, etc. Sodium also occurs combined with fluorine and aluminum fluoride as cryolite. In small proportions sodium salts occur in coal, limestone, dolomite, and other minerals, as well as in solution in the water of rivers and mineral springs. In plants sodium occurs as sulphate, iodide, and chloride, and combined with vegetable acids, especially in some kinds of sea-weed, and in certain plants which grow near the sea, such as salicornia, salsola, and chenopodium, etc.; in animals sodium occurs as chloride, phosphate, carbonate, and sulphate, and combined with various organic acids.

Characters.—Sodium is a solid substance possessing all the essential characters of a metal; it has a dull silver-white colour and considerable lustre when the surface is clean, but it soon becomes dull by oxidation. The density of sodium is less than that of water, its specific gravity being about 0·972. At the ordinary temperature sodium is soft, and can be easily cut with a knife; when cooled to 0° it is ductile, and at −20° it becomes much harder; it melts between 96° and 97°, and is volatilisable at a higher temperature. When exposed to the air, sodium gradually oxidises, and when heated in contact with atmospheric air, it burns with a yellow flame, forming sodium monoxide Na_2O, and sodium peroxide Na_2O_2; heated in oxygen gas the peroxide only is formed. Sodium decomposes water with evolution of hydrogen gas and formation of sodium hydrate NaHO, which dissolves in the excess of water.

Preparation.—Sodium is obtained by exposing to a very high temperature a mixture of dry sodium carbonate and charcoal or coal. The reaction that takes place consists in the formation of carbonic oxide, with reduction of the sodium, as shown by the following equation:

$$\underset{106}{Na_2CO_3} + \underset{24}{2C} = \underset{84}{3CO} + \underset{46}{2Na}$$

Deville recommends adding to the mixture some porous material, such as chalk, to prevent the separation of the melted sodium carbonate from the charcoal, and he gives the following proportions:

Dry sodium carbonate	30	parts by weight.
Charcoal or coal	13	„ „
Chalk	3	„ „

According to Tissier, the addition of chalk is unnecessary when the proportion of charcoal is properly adjusted.

The materials must be well dried, powdered, and thoroughly mixed in such a way as to avoid absorption of moisture. In making sodium on a small scale a mercury bottle may be used for heating the mixture, and fitted in a furnace, as shown in fig. 134.

The end of the mercury bottle (A) is supported by a firebrick (B), and into the neck of the bottle (C) is fitted a short iron tube, by which the sodium vapour is passed into the condenser (D E).

In preparing sodium on the large scale, the mixture is heated in wrought-iron tubes about four feet long and five inches wide, closed at both ends with wrought-iron lids, in one of which is a hole for screwing in the delivery tube by which the sodium distills off. The tubes are covered with clay and laid in fire-clay cases in a reverberatory furnace with good draught, in such a way that the ends slightly protrude. The space between the iron tube and the fire-clay cases is filled in with powdered fire clay or some other fire-resisting material. For setting the process going, the iron tubes are first made very slightly red hot, and then the non-perforated lid is removed, and the mixture, packed in paper cartridges, is introduced, each tube holding about ten pounds of the mixture.

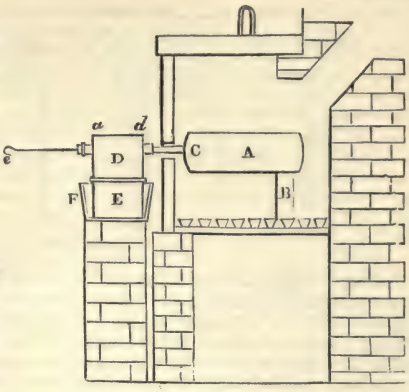


FIG. 134.

A number of tubes of the kind are laid side by side in the furnace. The lids are then again screwed on to the tubes, smeared over with clay, and the tubes are heated to bright redness. After the escape of some water vapour, combustible hydrocarbons are given off with carbonic oxide, etc., and finally vapour of sodium, which may be recognised by its forming a thick fume in contact with the air (sodium carbonate) and burning with a yellow flame. Directly large quantities of sodium vapour are observed to come off, the delivery tubes are screwed in and connected with a wide condenser, in which the sodium vapour condenses and drops in the form of metallic sodium into vessels placed beneath, half filled with petroleum. The crude sodium is then melted under petroleum, and cast into bars for the market.

The condensers, which contain considerable quantities of sodium, are cleaned by holding them beneath petroleum, and scraping off the sodium with some sharp instrument. The impure residues found in the receivers are purified by distilling them from a mercury bottle.

A couple of tubes of the above dimensions, holding together 24 pounds of sodium mixture, yield about 42 ozs. of raw sodium, from which 38 ozs. of pure product may be obtained.

When upon protracted heating sodium vapour ceases to be given off, the receivers are removed, the retorts or tubes opened, the residue removed, and the tubes recharged.

Owing to the fact that sodium rapidly oxidises in contact with air and moisture, it requires keeping under petroleum.

SODIUM OXIDE.

FORMULA Na_2O. MOLECULAR WEIGHT 62.

This substance closely resembles the corresponding potassium compound, and it is formed in the same manner.

SODIUM HYDRATE.

FORMULA NaHO. MOLECULAR WEIGHT 40.

Characters.—Caustic soda as usually met with is a white translucent crystalline mass, which rapidly attracts moisture from the air, and is readily soluble in water; even at the highest temperatures no water can be driven off from the fused substance, and it volatilises without decomposition. The solution of sodium hydrate in water is accompanied by rise of temperature. After deliquescing caustic soda soon becomes hard again from formation of sodium carbonate. Aqueous solutions of it when cooled

to 0° deposit a crystalline hydrate containing $Na_2O.8H_2O$. The amount of caustic soda in aqueous solutions may be ascertained from their specific gravity, which increases with the amount of caustic soda dissolved, as shown in the following table:—

Spec. Grav.	Per Cent.	Spec. Grav.	Per Cent.
2·00	77·8	1·40	29·0
1·55	63·6	1·36	26·0
1·72	53·8	1·32	23·0
1·63	46·6	1·29	19·0
1·56	41·2	1·23	16·0
1·50	36·8	1·18	13·0
1·47	34·0	1·12	9·0
1·44	31·0	1·06	4·7

Pure caustic soda, when dissolved in water, forms a clear colourless liquid that has a strong alkaline reaction and caustic taste; it dissolves fats, and forms saline compounds with the acids they contain—a process technically termed saponification. When exposed to the air caustic soda absorbs carbonic acid, and therefore solutions of caustic soda require to be kept in well-stoppered bottles. Sodium hydrate is also soluble in alcohol; the solution when freshly prepared is colourless, but gradually becomes brownish, and eventually black in colour, owing to the formation of a resinous substance.

Preparation.—Sodium hydrate, or caustic soda, may be prepared on the small scale by dissolving crystallised soda (sodium carbonate) in four times its weight of water, in an iron or silver vessel, and adding one-fourth its weight of lime mixed with four times its weight of water. This mixture is boiled until carbonic dioxide has been entirely abstracted by the lime, and a small quantity of the liquid filtered from the suspended calcium carbonate no longer effervesces when treated with a dilute acid. This indicates that the whole amount of sodium carbonate has been converted into hydrate, the reaction taking place according to the equation:

$$\underset{106}{Na_2CO_3} + \underset{74}{CaH_2O_2} = \underset{80}{2NaHO} + \underset{100}{CaCO_3}$$

The clear liquor in the pan is then filtered or decanted from the calcium carbonate, and either at once filled into well-stoppered bottles, or evaporated to dryness in silver or iron dishes. This method was formerly employed for the preparation of caustic soda on the large scale.

Caustic soda is now produced, together with sodium carbonate, by Leblanc's method, the quantity of coal added to the mixture of sodium sulphate and chalk being increased in order to obtain more of the soda in the caustic state. After the liquor obtained by the lixiviation of the ball soda has cleared, it is at once concentrated to a specific gravity of 1·5, the sodium carbonate which separates is removed, and the mother liquor heated in iron vessels to about 150°. Some Chili saltpetre (sodium nitrate), amounting to from 3 to 4 per cent. of the caustic soda in the liquor, is then thrown in for the oxidation of the sulphides, hyposulphites, and sulphites of sodium present in the liquor. The nitrogen of the sodium nitrate escapes partly as ammonia and partly in the free condition, according to the following equations:

$$Na_2S + NaNO_3 + 2H_2O = Na_2SO_4 + NaHO + NH_3.$$
$$5Na_2S + 8NaNO_3 + 4H_2O = 5Na_2SO_4 + 8NaHO + 8N.$$

The sodium nitrate causes further the decomposition of cyanogen compounds (sodium ferrocyanide) and the conversion of ferrous sulphide into ferric oxide, which collects at the bottom of the pans, together with other impurities. The clear liquor is then drawn off, concentrated to a spec. grav. of 1·9, and run into cylindrical or rectangular cast-iron moulds, in which it solidifies to a crystalline mass.

The use of atmospheric air as an oxidising agent in place of sodium nitrate is of considerable importance. It is forced into the solution either by means of an air pump or by steam. An arrangement of the kind much employed in this country consists of a cylindrical boiler furnished with a perforated false bottom at a little distance above its bottom. A tube at right angles to the axis of the cylinder, furnished with a funnel at its upper extremity and fitted into the middle of the false bottom, serves for charging the liquor with steam and air, which is effected by allowing steam to escape from a tube just above the mouth of the funnel. Steam mixed with air is thus brought beneath the false bottom, the mixture serving at the same time to heat the liquor and

oxidise impurities. The admission of steam and air is continued until the liquor no longer yields a precipitate of lead sulphide when a portion of it is treated with a solution of lead acetate.

A great number of other methods have been proposed for the preparation of caustic soda, among which the following may be mentioned. A process that has been several times patented consists in decomposing an aqueous solution of sodium sulphate with caustic baryta. Another method consists in first decomposing common salt with fluosilicic acid, the sodium silico-fluoride being then converted into caustic soda, by treating it with caustic lime, either at once, or after heating it to redness. When the sodium silico-fluoride is heated to redness, it is decomposed into sodium fluoride and gaseous silicium fluoride, which is converted into fluosilicic acid by passing it into water. Jean melts together fluor spar, calcium carbonate, Glauber's salt and carbon, the product upon treatment with water yielding a solution of sodium fluoride, which is then converted into caustic soda either by means of caustic lime or by superheated steam. Prückner suggests heating sodium sulphate to redness with coal, lixiviating out the sodium sulphide, and then decomposing it with copper scales. In this way caustic soda and cupric sulphide are formed (*vide* p. 268). Bachet recommends treating a solution of common salt with lead oxide, by which means insoluble lead oxychloride and sodium hydrate are formed. The oxychloride is then reconverted into soluble lead oxide by treating it with milk of lime.

Pure sodium hydrate is prepared by treating metallic sodium very carefully with a small quantity of pure water in bright iron or silver vessels. The product consists of a thick paste of sodium hydrate, which is dried and afterwards melted.

The percentage of sodium hydrate in commercial caustic soda varies considerably. Common caustic soda is always found to contain a number of foreign admixtures, and besides this the percentage of water contained in it varies with the degree to which the caustic soda liquor has been evaporated.

The following analyses of commercial caustic soda are given by Tissandier:—

	English Caustic Soda.			French Caustic Soda.		
	I.	II.	III.	IV.	V.	VI.
Sodium hydrate . .	87·73	87·50	85·71	75·31	72·65	86·10
,, carbonate .	3·45	3·68	5·48	5·58	9·82	3·69
,, sulphate .	1·00	1·32	2·10	3·41	2·00	2·60
,, chloride .	7·23	6·82	5·60	11·32	12·32	3·90
Water . . .	0·59	0·68	1·11	4·38	3·31	3·71

Besides the above substances, commercial caustic soda often contains small quantities of sodium hyposulphite, calcium carbonate, and other impurities.

Uses.—One of the chief uses of caustic soda is in soap making. It is also used in the place of soda in dye works, for removing fatty and other impurities from the stuff. Caustic soda is further used for purifying carbolic acid, petroleum, and coal oil products, etc., in the manufacture of oxalic acid and soluble glass, as well as for many purposes in the laboratory.

SODIUM CHLORIDE.

Formula NaCl. Molecular Weight 58·5.

History.—This important substance, generally termed common salt, has been known from the earliest times as being a necessary adjunct to the food of animals, and it is mentioned in the writings of Moses and Homer. In a chemical point of view it is interesting as constituting the type of a large class of substances now comprised under the generic term of salts. The Greek name of salt, ἅλς, denotes the solid substance left when sea water is evaporated, and the several steps by which this specific application of the term was extended show that the idea indicated by the etymology of the word led to its application to other substances obtained in like manner by the evaporation of watery liquids. Thus the residue left on evaporating the lye of wood ashes was termed a salt by Aristotle, and several other substances were designated by the same term with specific reference to their origin, as in the cases of *sal vegetabile* (potash), *sal ammoniac*, *sal petræ*, etc.

Occurrence.—Sodium chloride is one of the most widely distributed substances. It occurs in large and extensive beds in all parts of the earth, and in the most various

rock formations, being nearly always accompanied by clay and gypsum. Beds of rock salt, of large dimensions, occur in the Muschelkalk strata in Austria, in Würtemberg, Baden, Upper Bavaria, Hanover, etc. Rock salt is found in England in the red sandstone in Derbyshire, Worcestershire, etc.; it is found among the tertiary strata in the Carpathians, Hungary, and Galicia; also in Zeckstein, to which belongs the extensive rock salt bed formation north of the Harz mountains at Stassfurt, and south of the Harz at Erfurt, and other beds in Brandenburg, the Teutoburger forest, and other places in Germany. Rock salt occurs also in the chalk, Keuper and lias formations.

Sodium chloride occurs naturally as an efflorescence from the earth's surface, as for instance in the vicinity of the Caspian Sea, the tableland of Thibet, etc. Sodium chloride also occurs very abundantly in a state of solution in the water of a number of springs (salines), in the water of the sea, and in small quantities in all kinds of natural water.

Characters.—Sodium chloride, when pure, is a solid white substance, crystallising in cubes, but without water of crystallisation. It is hygroscopic only when it contains foreign ingredients, such as calcium chloride and magnesium chloride. The crystals of common salt, obtained by evaporating its solutions, are proportionally larger when the evaporation has been slow, appearing then as hollow quadrilateral pyramids with terrace-like sides, which are found upon examination to consist of aggregations of distinct cubes. Although the crystals of sodium chloride contain no water of crystallisation, they generally contain small quantities of mother liquor enclosed in them, and this causes the crystals to decrepitate when heated. Sodium chloride when strongly heated melts to a transparent colourless liquid; at a red heat it volatilises, and does so more readily when a current of air is passed over the heated mass. The solubility of sodium chloride in water does not vary much with the temperature: 100 parts of water at 15° dissolve 32·73 parts of sodium chloride; at 0° 35·52 parts; at 25° 36·13 parts; at 70° 37·88 parts; and at 100° 39·61 parts. A concentrated solution of salt, cooled down to − 15° deposits hydrated crystals, having a composition represented by the formula $NaCl + 2H_2O$, which however give up their water of crystallisation when the temperature is raised to − 10°. Sodium chloride is soluble in aqueous alcohol, in proportion to the amount of water it contains. It has a spec. gravity of from 2·10 to 2·15 and its taste is saline and pleasant.

Preparation.—Rock Salt.—The salt of the various rock salt deposits is seldom chemically pure, but always contains some admixtures of other salts, as may be seen from the following table of analyses:

	Sodium Chloride	Potassium Chloride	Calcium Chloride	Magnesium Chloride	Sodium Sulphate	Calcium Sulphate	Magnesium Sulphate	Potassium Sulphate	Manganous Chloride	Clay and Iron Oxide
Wieliczka	100·00	—	—	traces	—	—	—	—	—	—
Berchtesgaden	99.85	—	traces	0·15	—	—	—	—	—	—
Hall, Tyrol	99·43	—	0·25	0·12	—	0·20	—	—	—	—
Schwäb. Hall	99·63	—	0·09	0·28	—	—	—	—	—	—
Vic. Lothringen	99·30	—	—	—	—	0·50	—	—	—	0·20
Erfurt	98·04	traces	0·41	0·06	—	1·48	—	—	—	—
Cordona	98·55	—	0·99	0·01	—	0·44	—	—	—	—
Djebel Melah (Arabia)	97 00	—	—	—	—	3·00	—	—	—	—
Vesuvius 1822	83·10	13·90	—	—	1·60	0·70	—	—	—	—
„ 1850	62·45	37·55	—	—	—	—	—	—	—	—
„ 1855	94·30	—	—	—	0·20	0·70	0·40	1·00	0·60	—

It often happens that rock salt contains gases enclosed within it. Some specimens of rock salt from Wieliczka, for instance, decrepitate when thrown into water, owing to the escape of condensed gas, which has been found to consist of hydrogen, carbonic oxide, and marsh gas, olefiant gas sometimes replacing the latter. In some places rock salt is found together with petroleum.

Rock salt, according to its mode of occurrence, is either quarried or mined. In places where the deposit lies deep and is of great extent, large cavities are formed by

blasting, one over the other, which are supported by pillars and walls of the salt itself, as is the case in the enormous salt mine at Wieliczka.

Rock salt as it comes from the mine varies in purity. It is sometimes so pure and white that it requires no preparation but grinding to convert it into snow-white culinary salt. The more impure sort is, however, often lixiviated in suitable boilers with natural or artificial brine, and the solution evaporated to obtain the salt.

From Natural and Artificial Brine Springs.—Natural brine springs contain a sufficient amount of salt to render it profitable to boil the brine down at once. Springs of this kind are however rare, owing to the infiltration of surface water, which dilutes the brine. This dilution by surface water is prevented by means of water-tight shafts, which reach down to the spring. The more general plan is to bore a hole right into the bed of rock salt, and to pump from it a more saturated brine.

Artificial Brine Springs.—These differ from one another according to their situation, but they are all formed either by treating salt deposits themselves, or salt that has been already quarried, with fresh water, or with weak brine, which contains too little salt for boiling down. Thus brines are formed by boring into deposits of rock salt, and admitting water, generally surface water, the brine being then removed either with buckets or by pumping. The brine thus obtained contains about 20 per cent. of salt. Another method consists in lixiviating already quarried salt, the latter being generally impure from admixtures of clay and gypsum. The lixiviation is generally carried out at the surface, and seldom in the mine itself. The salt is treated in large boxes or pans, either with fresh water or with a weak brine; in some places sea water is used. The amount of salt in the brine thus obtained varies between 20 and 25 per cent.

The composition of brine varies considerably. The chief constituent is sodium chloride or common salt, but it always contains some other salts in solution, which considerably affect the value of the brine.

In the following table is given the analyses of brine from a few natural springs.

	Halle	Schönebeck.	Dürrenberg	Kreuznach
Sodium chloride	17·718	9·623	6·599	1·415
Potassium chloride	0·166	0·007	0·008	0·006
Sodium sulphate	—	0·249	0·208	—
Potassium sulphate	—	0·014	0·004	—
Calcium chloride	0·134	—	—	0·261
Magnesium chloride	0·406	0·083	0·092	0·023
Calcium sulphate	0·466	0·339	0·250	—
Magnesium sulphate	—	0·012	—	—
Calcium carbonate	—	0·026	0·058	0·003
Iron carbonate	—	0·001	0·004	0·005
Magnesium carbonate	—	—	—	0·001
Alluminum sulphate	—	—	—	0·001
Silica	—	—	—	0·013
Organic substance	—	0·001	0·012	traces

The following table gives the composition of a few artificial brines, which are as a rule richer in sodium chloride than the natural ones.

	Friedrichshall	Boring at Artern	Rappenau
Sodium chloride	25·563	23·652	25·850
Potassium chloride	—	0·112	—
Potassium sulphate	—	0·272	—
Calcium chloride	—	—	0·085
Magnesium chloride	0·006	0·395	0·042
Calcium sulphate	0·437	0·375	0·413
Magnesium sulphate	0·022	—	—
Calcium carbonate	0·010	—	0·001

For determining the percentage of salt contained in brine, gauges are used which indicate either the specific gravity of the brine, or the number of pounds of salt contained in a cubic foot of the brine. For finding the percentage of salts from the specific gravity of the brine, the following table by Bischof is used. The calculations are for a temperature of 15°

Spec. Grav.	Per cent. of Sodium Chloride.	Spec. Grav.	Per cent. of Sodium Chloride
1·00712	1	1·10323	14
1·012472	2	1·11095	15
1·02146	3	1·11872	16
1·02868	4	1·12655	17
1·03594	5	1·13443	18
1·04324	6	1·14327	19
1·05058	7	1·15038	20
1·05796	8	1·15844	21
1·06539	9	1·16657	22
1·07286	10	1·17476	23
1·08038	11	1·18302	24
1·08795	12	1·19135	25
1·09556	13	1·19975	26

In using this table, however, regard must be had to the fact that the presence of other salts than sodium chloride influences the specific gravity of the brine, and that too in a way different to sodium chloride; on which account the table can only be used for brine containing small quantities of other salts. The table, when used for brines containing large quantities of foreign salts, requires a correction, which varies with the brine, but is constant for one and the same brine, since in the latter case the relative amounts of the salts remain the same.

The strength of brine is sometimes expressed by the quantity of water which holds in solution one part by weight of salt. The measuring of brine is effected in various ways: in measuring boxes; in the receivers and evaporating pans, the capacity of which is known; or by observing the length of time occupied by the flow of the brine from tubes of known diameter.

Concentrating the Brine.—A great number of brines contain too little common salt in solution to enable them to be boiled down at once. Such brines are, therefore, subjected to a process of concentration, or what is technically termed gradation.

Faggot Gradation.—This operation, which is also known as drop gradation, is that most often employed. The weak brine is caused to trickle down the sides of a gradation house, which consists of a framework of timber fitted with faggots of the sloe (*Prunus spinosa*). The weak brine is pumped into a water-tight tank placed above the gradation house; this tank is provided with a number of taps from which the brine trickles into channels provided with holes to admit of its falling on the faggots. The entire construction is built over a water-tight tank which receives the concentrated brine. According to the way in which the gradation is conducted, the operation has received different names:—1. Surface gradation, in which the brine trickles down that side of the gradation house which is most exposed to the prevailing wind. 2. Cubical gradation, in which the brine drops down both outer sides, as well as both inner sides of the gradation house. 3. Combined cubic and trilateral gradation. This kind of gradation is the most effectual. Two gradation walls are placed side by side at a slight distance apart. The brine trickles down both the sides and the interior of that wall which is exposed to the prevailing wind, as well as over the exterior of the other wall which is placed near it. The brine, after having passed over the sides of the gradation house, is again pumped up into the dropping tank above, until it has attained the necessary concentration. It is, however, not customary to allow the brine to drop a second time over the same part of the gradation house, which is divided into 1st gradation, 2nd gradation, 3rd gradation, etc.; the first gradation receiving the fresh brine, the second gradation brine which has undergone one concentration, and the third gradation receiving brine which has been twice concentrated, etc. The brine is pumped up either by the aid of steam, water, or wind.

Figs. 135 and 136 represent the gradation house at the salt works of Dürrenberg. *c c* are the inner walls of thorn faggots, *d d* are the outer walls, both being 18 inches thick. At the top of the thorn walls are the brine spouts (*o o*), with the dropping spouts (*p p*) for distributing the brine over the walls by the spigots (*s s*), as shown on a larger scale by fig. 137. The brine cistern (*b b*) over which the walls are built is supported upon brick walls (*a a*).

The gradation process not only serves the purpose of concentration, but also that of purifying the brine, as some of the foreign salts are deposited on the faggots. The first gradation generally seems to separate calcium carbonate, owing to the escape of

carbonic acid which retained that salt in solution as acid carbonate. The other gradations cause chiefly a deposit of gypsum. The salts deposited are called by the Germans



Fig. 137.

Fig. 135.

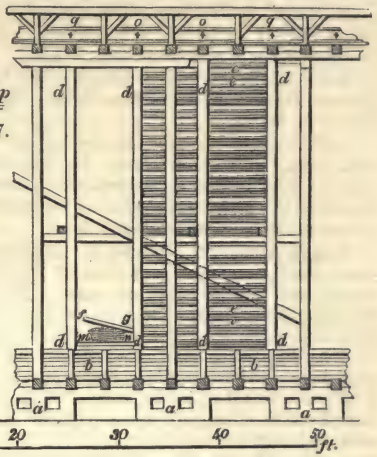


Fig. 136.

thornstone. The following table gives the composition of such thornstones from the salines of Schönebeck and Dürrenberg.

	Schönebeck			Dürrenberg	
	I. Grad.	II. Grad.	III. Grad.	I. Grad.	II. Grad.
Calcium carbonate	83·166	1·492	0·924	0·612	0·113
Calcium sulphate	3·540	95·322	96·138	97·444	98·748
Sodium chloride	2·957	1·669	1·350	0·155	0·438
Sodium sulphate	2·286	0·087	0·346	0·197	—
Potassium sulphate	0·904	0·756	0·592	0·586	0·398
Magnesium carbonate	1·745	0·275	0·204	0·125	0·084
Aluminum sulphate	—	—	—	0·555	—
Ferric oxide	2·104	0·094	0·077	0·136	—
Alumina	0·499				
Silica	2·499	0·300	0·324	0·190	0·219

In the course of a few years the deposit becomes so thick, that the faggots require renewing, and the old ones are sometimes used as manure.

The gradation of the brine causes a considerable loss of salt, which is carried away by the wind.

The concentrated brine which is left in pits or basins to settle, yields a further precipitate consisting chiefly of calcium carbonate and sulphate.

The concentration of graduated brine varies at different works, and the amount of salt is generally between 17 and 25 per cent., sometimes as high as 27 per cent.

The composition of the brine used for boiling down at the Schönebeck salines is given in the following table:

	I. Grad.	II. Grad.	III. Grad.	IV. Grad.
Sodium chloride	15·48	19·09	23·54	25·16
Potassium sulphate	0·23	0·28	0·36	0·55
Calcium sulphate	0·49	0·46	0·38	0·17
Magnesium sulphate	0·11	0·23	0·23	0·61
Magnesium chloride	0·14	0·15	0·19	0·63

There are also other methods of gradation, as already mentioned, but they are little suited for working brine.

Gradation by Freezing.—This method is practised on the coast of the sea of Okotsk and at Irkutsk in Siberia. The water is allowed to freeze, and the ice removed, a strong solution of salt remaining.

Solar Gradation.—This method is chiefly used for concentrating sea water, seldom, however, for preparing salt from brine. The water is allowed to evaporate in the sun in shallow basins.

Table Gradation consists in causing the brine to flow slowly down a number of steps formed of shallow boxes. *Roof gradation* is a similar process, the brine being made to flow over inclined surfaces like the roof of a house. *Rope gradation* consists in passing the brine over vertical ropes, upon which it forms a crystalline deposit that is scraped off when sufficiently thick.

Boiling down.—This process is carried out either in hemispherical or flat pans. Those usually employed are formed of sheet-iron plates riveted together, and are in shape round, hemispherical, or square. The most convenient size is between 600 and 1000 square feet area. The pans are heated by hot air made to circulate beneath them from a furnace. A suitable chimney conducts the vapour into the air.

According to the purity of the brine, the boiling down is performed in one or two operations. Brine containing large quantities of gypsum or sodium sulphate is first of all concentrated in special pans until these impurities separate, together with some ferric hydrate, silica, and sodium chloride in the form of mud. The heating is then continued until a crust of salt has formed on the surface, indicating that the liquor is saturated. The clear liquor is then drawn off into other pans and evaporated until the salt crystallises out, the crystals being removed as formed and placed on a board near the pan to drain. Each time a portion of crystallised salt is removed, a fresh quantity of brine is let into the pan, the operation being continued until the mother liquor is too impure to yield a further crop of sufficiently pure salt. The mother liquor is then either thrown away or treated for other products.

Fine-grained salt is obtained at a temperature of 90°–100°, coarse-grained salt at a temperature between 60° and 70°. The salt separated decreases in purity during the process of crystallising. At the beginning of the operation, salt is obtained containing 95 or 96 per cent. of sodium chloride, and towards the end of the operation the amount of salt is only 80 per cent. The quantity of salt separated in a given time is greater in proportion to its coarseness, being for fine-grained salt 20 to 25 lbs., and for coarse-grained salt only 25 to 25½ lbs. per square foot in twenty-four hours.

The sheet-iron pans are replaced in many districts by cast-iron pans made in sections, the flanges of which are fixed together by bolts; they are more durable and also cheaper than sheet-iron pans.

Wooden evaporating pans are but seldom used; they are made of fir planks and the brine is heated by means of copper tubes through which superheated steam is passed.

Another kind of evaporating pan is made of brickwork, and the brine is evaporated by passing hot air from a fire over its surface. It is necessary in this case that the pan should be arched over, and this renders the operation so difficult that these pans have not been much employed.

Drying of the Salt.—The operation of drying the salt is effected either in the open air or in specially constructed drying chambers that are kept at a temperature of 50°–60°, either by means of the hot air from the evaporating pans, or by a separate heating arrangement. The salt is laid out in the chambers either upon wooden shelves in layers of 3½ to 5 inches in depth, or in the perforated boxes or baskets in which it was placed to drain.

Instead of drying chambers, drying hearths or pans are sometimes used, the bottom of which is made of limestone slabs or sheet iron. They are heated from beneath by the hot air or vapour of the boiling pans.

Box Drying.—The salt is spread out upon hurdles contained in wooden boxes, hot air being passed into the boxes from below. The air is heated in tubes lying in the hearth of the boiling pans.

In some districts of Transylvania salt is dried over an open fire, the salt being for this purpose moulded into forms like sugar cones.

In drying salt care must be taken to avoid too high a temperature, for if it is too high gypsum loses its water and becomes insoluble, and, further, magnesium chloride is partly converted into insoluble magnesia.

The composition of the salt obtained from different salines may be seen from the following table:

	Wimpfen	Schwäb. Hall	Halle	Neu Salzwerk	Ischl
Sodium chloride	99·45	98·90	98·36	91·35	87·39
Sodium sulphate	0·05	0·005	—	1·00	1·25
Calcium chloride	—	—	—	—	—
Magnesium chloride	—	—	0·28	0·39	2·06
Calcium sulphate	0 28	0·49	1·33	0·57	0·35
Magnesium sulphate	—	—	—	—	0·43
Magnesium carbonate	—	0·005	0·03	—	—
Water	—	0·60	—	6·68	7·91
Organic matter	—	—	—	—	0·35

An impure salt containing a considerable amount of gypsum (1–4½ per cent.) and organic substance is used for cattle.

In some countries where salt is an article upon which an excise duty is levied, in order that it may be employed duty free for certain industrial purposes, common salt is often mixed with substances which render it unfit for culinary use, such as gypsum, Glauber's salt, green vitriol, charcoal, ashes, etc., and it is then termed *denaturalised salt*. The substances added are selected according to the ultimate use of the salt—for cattle, for manure, or for industrial purposes.

The pan scale which adheres to the vessels in which salt is boiled down is especially rich in gypsum, but it also contains considerable quantities of common salt. The pan scale of the Halle salines has the following percentage composition:

Sodium chloride	29·028
Potassium chloride	1·310
Calcium chloride	2·431
Magnesium chloride	0·243
Calcium sulphate	62·981
Calcium carbonate	1·265
Magnesium carbonate	1·905
Ferric oxide and alumina	0·304
Silica	0·533

Pan scale from other salines has been found to contain, besides the above ingredients, sulphates of sodium, potassium, and magnesium.

Pan scale is either treated for common salt or used as manure, or in the manufacture of green glass.

The mother liquor of brine from which the sodium chloride has been extracted varies considerably in composition, and is treated accordingly for various products, the saline constituents being extracted by fractional crystallisation. When the mother liquor contains bromine or iodine, it is often dried and used as bathing salt.

Salt from Sea Water.—The essential constituents of sea water do not differ in any part of the world, and the difference in quantity is very small, as may be seen from the following table:

	German Ocean	Atlantic Ocean	Pacific Ocean	Mediterranean Sea	Red Sea
Sodium chloride	2·5513	2·7558	2·5877	2·9424	3·030
Potassium chloride	—	—	—	0·0505	0·288
Sodium bromide	0·0373	0·0326	0·0401	0·0556	0·064
Potassium sulphate	0·1529	0·1715	0·1359	—	0·295
Calcium sulphate	0·1622	0·2046	0·1622	0·1357	0·179
Magnesium sulphate	0·0706	0·0614	0·1104	0·2477	0·274
Magnesium chloride	0·4641	0·3260	0·4345	0·3219	0·404
Calcium carbonate and ferric oxide	—	—	—	0·0117	—

The method of obtaining common salt from sea water varies according to the locality.

The most important and also the most general method which is adopted in the South of France, Spain, Portugal, Southern Italy, Sicily, Istria, and Dalmatia, etc., consists in evaporating the sea water in a series of pits or basins called a *salt garden*. The sea water is passed first of all into basins of large capacity, and somewhat deep, where it is allowed to stand some time so as to deposit mechanical impurities. The

clear water is then drawn off into a system of basins, each successive basin being shallower and smaller than the one before it. The basins are excavated in the ground and are separated from each other by thin clay walls. The sea water, after having passed through the first set of basins, has a specific gravity of 1·152, and the water in the last of the smaller basins has a gravity of 1·197. The following table gives the amount and nature of the foreign substances precipitated from sea water during its concentration in the basins from sp. gr. 1·034 to 1·197, at the different degrees of concentration :—

10,000 parts of sea water deposit at a specific gravity of 1·049 of			Ferric hydrate .	0·031 parts.
			Calcium carb. .	0·672 „
„	„	1·122 of	Calcium carbonate, with a little magnesium carbonate .	0·530 „
„	„	1·122 of	gypsum . . .	5·600 „
„	„	1·156	„ . . .	5·600 „
„	„	1·169	„ . . .	1·800 „
„	„	1·197	„ . . .	1·600 „

The liquor having attained a specific gravity of 1·19, is passed into still smaller and shallower basins, and in proportion as the sodium chloride deposits, it is raked out from time to time and laid in small heaps to drain; when dry, it is packed in sacks for the market.

Usiglio gives the following table for the deposition of sodium chloride and other salts from sea water at different degrees of concentration between sp. gr. 1·197 and 1·245.

Specific gravity	10,000 parts of water originally taken are reduced to	There is separated out				
		Gypsum	Sodium chloride	Magnesium sulphate	Magnesium chloride	Sodium bromide
	parts	parts	parts	parts	parts	parts
1·208	950	0·508	32·614	0·040	0·078	—
1·216	640	1·476	96·500	0·130	0·356	—
1·247	302	0·144	26·240	0·174	0·150	0·358
1·271	230	—	22·720	0·254	—	0·518

Treatment of the Mother Liquor.—The mother liquor of sea water, after the chief part of the sodium chloride has been removed, is in some places thrown into the sea, while in other districts it is treated for various by-products.

In the South of France the mother liquor, having a specific gravity of 1·267, is concentrated to sp. gr. 1·299, so as to deposit in one or two crystallisations magnesium sulphate and common salt in nearly equal parts. This mixture is dissolved in as little water as possible, and the liquor passed alternately into day and night receivers. During the day sodium chloride crystallises out, and during the night magnesium sulphate, together with a double salt of potassium and magnesium sulphate containing 6 molecules of water. The mother liquor that has been drawn off from the deposit of sodium chloride and magnesium sulphate is then run into other vessels; when evaporated further it yields crystals of artificial carnallite ($KClMgCl_2 + 6H_2O$), which are then treated for potassium chloride by dissolving them in water and crystallising.

Porosity of the soil and change of weather are very unfavourable to the treatment of mother liquor by the above process; for when by concentration of the mother liquor it has attained a specific gravity of 1·299, very slight alteration in the amount of water or in the temperature during the night gives rise to the formation of very different products.

Payen recommends treating the mother liquor according to the method introduced by Merle in the salines of the island of Camargue and of Alais, by which the mother liquor, concentrated only to 1·968 specific gravity, is cooled by Carré's apparatus and treated for different products, as follows—

Separation of Sodium Sulphate.—The liquor is conducted from the reservoirs by subterranean tubes in any required quantity into vessels fitted with the ammonia tubes of Carré's freezing apparatus, water being added in quantity sufficient to prevent the crystallisation of sodium chloride with the sodium sulphate. The liquor is cooled by passing it through tubes lying in a liquor cooled to $-18°$ in a previous operation, so that it comes into the freezing vessel cooled to a temperature of $-10°$, and it is then further cooled by the tubes of Carré's machine to a temperature of $-18°$.

The effect of this cooling is that about 85 per cent. of the sodium sulphate present separates in the crystalline condition, and is removed with cullenders attached to an endless chain, the adherent water being separated in a centrifugal machine. The sodium sulphate is finally calcined, the salt being generally used in this state.

Separation of the Residual Sodium Chloride.—The mother liquor obtained in the last operation is saturated with sodium chloride by filtration through raw sea salt, and it is then boiled down for common salt in the usual way. The product thus obtained, after being washed with a solution of sodium chloride to remove the magnesium chloride, is very pure.

Preparation of Potassium Chloride.—The mother liquor of the last operation, from which the sodium chloride has been extracted, having a specific gravity of 1·288, is run out into crystallising vessels, and after a short time crystals of artificial carnallite ($KClMgCl_2 + 6H_2O$) are deposited. From these crystals magnesium chloride is extracted, either by the aid of cold water alone, or by heating them with a small quantity of water, and then cooling the solution. The product thus obtained contains on the average 90 per cent. of potassium chloride, the remainder consisting of water, traces of magnesium chloride, and earthy admixtures.

Separation of Magnesium Chloride.—The mother liquor, freed from artificial carnallite and concentrated to sp. gr. 1·333, deposits upon cooling almost pure magnesium chloride in a crystalline condition; this salt is used for the preparation of freezing mixtures, or of pure hydrochloric acid, as well as for the prevention of dust in streets sprinkled with it. The property of preventing dust is due to its hygroscopic nature.

Preparation of Bromine.—The preparation of bromine from the final residues of the mother liquor of sea water has been already treated of on page 177.

Common salt obtained from sea water varies in composition, as may be seen from the following analyses:

	Charente Inférieure	Languedoc	Trapani, Sicily	St. Ubes, Portugal
Sodium chloride	96·42	95·11	96·35	95·19
Sodium sulphate	—	—	0·51	—
Magnesium chloride	0·20	0·23	0·50	—
Calcium sulphate	1·95	0·91	0·45	0·56
Magnesium sulphate	0·43	1·30	—	1·69
Insoluble matter	1·00	0·10	0·07	—
Water	—	2·35	2·12	2·45

Of the different kinds of salt obtained from sea water, that made in Portugal has the best repute; the salt of St. Ubes, especially, is very much sought after for pickling meat, fish, and the like. It was formerly supposed that this salt owed its character to the large amount of magnesium sulphate; but Payen considers that its physical consistency, its white colour, and compactness are the cause of this salt being so much liked. He remarks further that sea salt produced in France and England, when properly prepared, is just as good as that obtained from St. Ubes.

Uses.—Sodium chloride being a necessary ingredient of human and animal food, finds one of its most important applications as a condiment, to mix with the food of man and of cattle. It is also used for several agricultural purposes. Large quantities of salt are used in the preparation of soda by Leblanc's process, also in the preparation of hydrochloric acid, chlorine, sal ammoniac, corrosive sublimate, aluminum, sodium, etc. Salt is further used in the glazing of the coarser kinds of pottery and earthenware, in tanning, in soap works, etc.; as a preservative for wood, meat, fish, butter, etc.; it is also employed to some considerable extent in the laboratory for preparing freezing mixtures, etc.

SODIUM SULPHIDES.

Sodium combines with sulphur in several proportions, forming compounds represented by the formulæ Na_2S, Na_2S_2, Na_2S_3, Na_2S_4 and Na_2S_5. The latter substance is probably a constituent of ultramarine, and the monosulphide has been lately introduced into use in the preparation of hides for tanning.

ULTRAMARINE.

History.—Kopp considers it probable that ultramarine or lapis lazuli is identical with the sapphire of the ancients. The word 'lazur,' meaning blue, is said to be of Persian origin, and at any rate it is certain that the expression 'lazur' was used in the sixth century by Leontinus, a Greek author, as designating a blue pigment, and from his time it became very frequent. The first mention of the preparation of a blue pigment from lapis lazuli dates from the eleventh century; and at a later period it received the name of ultramarine, when the only source of the material was 'beyond the sea.'

The first imitations of ultramarine consisted in preparing blue glass fluxes; however, this product was far from being of sufficiently pure or deep colour. For a long time it was generally supposed that the blue colour of ultramarine was due to copper; but this supposition was, however, disproved by Marggraff.

The art of preparing true artificial ultramarine dates from the beginning of the present century, as a result of the researches of Gmelin in Germany and Guimet in France. The priority of the discovery is claimed by both chemists. It has, however, been ascertained that Gmelin in 1827 informed Gay-Lussac of his discovery, and was induced by him to keep the discovery a secret. In 1828 Gay-Lussac gave an account before the French Academy of Guimet's discovery of artificial ultramarine, but kept secret his knowledge of Gmelin's previous researches.

Occurrence.—Ultramarine occurs naturally in lapis lazuli, a mineral found in different parts of China, Thibet, Siberia, etc.; and it was this mineral, reduced by mechanical means to a very fine powder, which was formerly brought into the market as ultramarine.

Composition.—The composition of natural ultramarine may be seen from the following analysis by Varrentrap:

Silica	45·50	Ferric oxide	0·86
Sulphuric acid	5·89	Sulphur	0·95
Alumina	31·76	Chlorine	0·42
Soda	9·09	Water	0·72
Lime	3·52		

Lapis lazuli is a very rare mineral, and for this reason the native ultramarine formerly prepared, at a time when the secret of preparing artificial ultramarine was unknown, was a very costly article.

Under the head of artificial ultramarine are distinguished two substances, green and blue ultramarine. The former admits of being converted into the latter, and is indeed usually nothing more than an intermediate product obtained in the preparation of the blue pigment.

The following analyses will serve to show the composition of different kinds of blue ultramarine: I. Meissner ultramarine (analysed by R. Wagner). II. Nuremberg ultramarine (analysed by Elsner). III. The same (Gentele). IV. and V. Blue ultramarine (analysed by Breunlein). VI. Ultramarine analysed by Wilkens.

	I.	II.	III.	IV.	V.	VI.
Silica	44·70	39·9	36·91	40·91	36·59	39·39
Alumina	25·62	30·0	29·17	24·19	25·05	26·40
Ferric oxide	0·53	0·9	1·01	0·50	0·91	—
Soda	21·65	25·5	21·25	16·28	17·20	21·52
Sodium	—	—	—	3·17	3·19	—
a. Sulphur*	7·24	4·6	5·90	2·20	2·22	12·69
b. Sulphur			—	8·45	8·68	
Sulphuretted hydrogen	—	—	0·93	—	—	—
Sulphuric acid	3·62	0·4	2·52	1·31	1·99	—
Lime	0·17	—	0·60	0·82	1·02	—
Clay	—	—	—	1·46	2·81	—

Green ultramarine has a composition as shown in the following analyses of Breunlein (I.) and Gentele (II.):

* *a.* Sulphur which upon treating the ultramarine with sulphuric acid separates out as sulphuretted hydrogen. *b.* Sulphur which, treated with the same reagent, separates as sulphur.

	I.	II.
Silica	38·39	37·82
Alumina	27·38	29·39
Ferric oxide	0·63	1·40
Soda	16·93	25·31
Sodium	5·29	—
a. Sulphur	3·68	3·00
b. Sulphur	3·49	3·64
Sulphuric acid	0·52	0·59
Lime	0·83	1·13
Clay	1·70	—

As to the mode in which the different substances of which ultramarine is composed are combined, or the chemical constitution of this substance, the most diverse views are held, and it is a matter of great difficulty to deduce from known facts any satisfactory representation on this point.

Breunlein and Böckmann consider blue ultramarine as consisting of silicates of sodium and aluminum with sodium pentasulphide.

Stein considers ultramarine as a mechanical mixture consisting essentially of aluminum sulphide and sodium silicate, the latter substance enveloping the particles of aluminum sulphide and protecting it from the action of atmospheric air.

The same chemist holds that the blue colour of ultramarine is not peculiar to the substance, but due to the optical relations of the ingredients it consists of. He considers that in the same way as an intimate mixture of various black substances with an opaque white matrix (such as finely divided lamp black and milk, or black paper behind a sheet of opalescent white glass) gives rise to a blue colour, so the blue colour of ultramarine is due to the molecular dispersion of black aluminum sulphide throughout a white matrix, the latter consisting essentially of sodium silicate mixed with small quantities of sodium sulphate and sodium sulphite, together with some undecomposed clay and calcium salts.

That ultramarine does not contain sodium hyposulphite was proved by Stein, by boiling ultramarine blue with copper sulphate. Copper sulphide was produced, but no sulphurous acid, which must have been a product of the reaction if the ultramarine had contained sodium hyposulphite.

The absence of polysulphides is also proved by the fact that the copper sulphide precipitated upon boiling ultramarine with copper sulphate contains no sulphur extractable by carbon bisulphide, while we know that when copper sulphate is made to act upon a polysulphide, the precipitate thus formed does contain sulphur extractable by carbon bisulphide.

The absence of sodium monosulphide has also been inferred by Stein, because when sodium monosulphide is fused together with sodium silicate a yellow colour is produced, which is not the case with ultramarine.

Characters.—Ultramarine when quite pure is a most beautiful impalpable blue powder insoluble in water. It is easily decomposed and bleached by weak acids, the decomposition being accompanied by an evolution of sulphuretted hydrogen. Salts having an acid reaction such as alum, etc. behave like acids with ultramarine.

Green ultramarine likewise occurs in the market as a fine powder. It is a pigment of comparatively little importance, the colour not being equal to that of copper salts.

The chief object in testing ultramarine is to ascertain its colouring power, *i.e.* the quantity requisite to produce a given shade. By comparison of the relative quantities of different samples of ultramarine required to produce a shade of a definite intensity, it is found that the amount required differs according to the quality of ultramarine. Of course the less the quantity of ultramarine required, the greater is its colouring power and relative value.

Barreswil's method.—Of two sorts of ultramarine to be compared with one another, a small quantity of each (0·5 – 1 gram) is accurately weighed in watch glasses. Two porcelain mortars are then separately charged with 20 grams of precipitated barium sulphate, and into one of them is thrown a portion of the ultramarine from one of the watch glasses, the whole being rubbed together to a homogeneous mass. A portion of the ultramarine in the other watch glass is then added to the barium sulphate in the second mortar, and rubbed with it until the whole mass has assumed a shade equal in intensity to that in the first mortar. Upon re-weighing the residual portions of ultramarine in the watch glasses, the relative quantity of ultramarine required to bring about the same intensity of colour is easily ascertained.

Bernheim's test.—This test consists essentially in ascertaining the quantity of dilute sulphuric acid of known strength required for decomposing and decolorising a definite quantity of the ultramarine to be tested. For this purpose 30 grams of sulphuric acid are diluted with 300 grams of water; two equal portions of the sample of ultramarine ($\frac{1}{3}$–$\frac{2}{3}$ grams) are then brought separately into two glass flasks, and the sulphuric acid dropped in, the flask being shaken meanwhile until every trace of blue has disappeared. The quantity of acid required to bring about the decolorisation of the ultramarine is in direct proportion to its colouring power, and the greater the quantity of acid required to bleach the ultramarine, the stronger is the colouring power of the ultramarine.

Ultramarine of good quality should be in the state of an impalpable powder that will mix with water to a fine mud, and upon stirring up with water must remain for some time suspended in that liquid. The dry powder, spread upon a sheet of paper with the finger, should give a continuous streak with even surface.

The value of ultramarine is also much influenced by the amount of fixing material necessary for causing it to adhere properly to paper; for since ultramarine loses in beauty of colour when a large proportion of fixing material is used, it is of relatively greater value when it requires least fixing material.

Another important requisite of ultramarine is that it should be 'alum proof;' for since alum is often used in blueing paper, the greater or less capability of ultramarine to resist the action of alum is of importance. Ultramarine may be rendered 'alum proof' by using a good deal of silicic acid in its preparation.

Preparation.—It is a matter of the utmost importance in preparing ultramarine that all the materials used should be as pure as possible; these consist of clay, Glauber's salt or soda, sulphur, and carbon.

Clay.—The best kind of clay for making ultramarine is kaolin or porcelain earth. If it contains sand, this must be removed by a process of elutriation. In order to render the clay sufficiently friable, it is first heated to redness and then reduced to a very fine powder by grinding. The powder is then passed through sieves so as to render it as impalpable as possible. Clay containing more than 1 per cent. of ferric oxide, and large quantities of lime and magnesia, is not suitable for use in the preparation of ultramarine.

Sodium sulphate.—This substance is used in the calcined state, and is met with in commerce sufficiently pure for the purpose. The chief points to be looked to, are that it does not contain either free acid, sodium chloride, ferric oxide, or lead sulphate. The calcined Glauber's salt is first pressed between rollers and afterwards passed through sieves, to bring it to a sufficiently fine state of division.

Soda.—Soda is often used instead of Glauber's salt, and the same degree of purity is required as in the case of the sulphate. It is also used in the calcined state, and in the form of a very fine powder.

Sulphur.—Roll sulphur is employed, which has been previously ground and passed through fine sieves.

Carbon.—Carbon is generally used in the form of soft wood charcoal; coal free from ash being sometimes, but comparatively seldom, employed. The charcoal is reduced to the desired state of division by passing it between rollers and then grinding the powdered charcoal with water to a fine paste between millstones. The fine paste or mud is then dried and passed through sieves. In some manufactories colophonium and other resinous substances are employed.

The following recipes are given by Wagner as the normal relative proportions of the ingredients used in preparing ultramarine:

	I.	II.
Porcelain clay (anhydrous) . . .	100	100
Calcined Glauber's salt	83–100	41
Calcined soda	—	41
Charcoal	17	17
Sulphur	—	13

But generally there is considerable diversity in the relative proportions of ingredients taken by different manufacturers. When ultramarine of a dark blue colour is desired, sodium sulphate is alone employed; soda yields ultramarine of a lighter and finer colour with more body; 100 parts of soda replacing about 80 of Glauber's salt.

Very frequently sodium sulphide, a by-product obtained in the manufacture, is

partly substituted for soda or Glauber's salt in making ultramarine, the proportion being 60 parts sodium sulphide for 100 parts sodium sulphate.

Not only is it necessary that the materials used in preparing ultramarine should be pure, but they must likewise be employed in a very fine state of division, and very intimately mixed together. The mixing is often carried out in drums similar to those employed in the manufacture of gunpowder.

After the ingredients have been thoroughly mixed in the proper proportions, the mixture is submitted to the following operations, and the character of the product depends very much upon the manner in which they are conducted.

Heating the ingredients.—The ingredients are generally heated in fire-clay crucibles 12 or 18 inches deep and about 6 inches wide. The composition, in a state of fine division and intimately mixed, is firmly rammed into the crucible, which is then covered with a lid and placed in the furnace. The furnaces are mostly muffle-shaped, and are often so built that the hot air from the furnace first passes under the sole of the muffle and then through it. The crucibles are heated to bright redness or incipient white heat, and this temperature is kept up for half a day. When they have been heated sufficiently, the crucibles are allowed to cool down in the furnace, and are then removed. It is essential to the success of the operation to prevent the access of any large quantities of atmospheric air during the heating process.

The contents of the crucibles are then broken up into small pieces, lixiviated with water, and eventually submitted to a process of elutriation. In this stage the material is in the state of ultramarine green, and is either sent as such into the market or is converted into ultramarine blue.

Burning of Ultramarine Blue.—The blue burning of ultramarine consists essentially of a roasting process, assisted or not, as the case may be, by the addition of sulphur. By this process a part of the sodium is extracted, and by the following operation of washing with water it is removed in the form of sodium sulphate.

For blue burning of ultramarine retorts or hearth furnaces are employed, which must, however, be so constructed that the mass may be stirred up without much air coming into contact with it, and that no access of hot air from the furnace is possible. So soon as the ultramarine green in the retort has attained a red heat, sulphur is thrown in, the whole mass being well stirred up. When the first portion of sulphur has burnt away, a second portion is added, and the operation is continued until a portion, on being taken out, presents the proper blue tint.

Lixiviation.—The next step is the lixiviation of the calcined mass in order to remove the substances rendered soluble, sodium sulphate being the principal one. The lixiviated mass is then ground between millstones, in what are called wet mills, and afterwards, by a process of elutriation, it is separated into ultramarine of different degrees of fineness. After some time has been given for the ultramarine to settle, it is first partially dried in clay boxes or linen sacks, with the aid of pressure, and then it is brought into a special drying room, and finally ground and passed through sieves.

When soda alone is used in the composition of the ingredients of ultramarine, larger masses are generally heated at a time in clay boxes, or the composition in form of a large block is laid direct upon the hearth of a reverberatory furnace, the hot air of the fire being made to pass under the hearth of the furnace, before it passes into the furnace. When the mass is sufficiently burnt, the furnace is closed, and the mass is allowed to cool down.

During the slow cooling a further roasting process takes place, by which the ultramarine is partly rendered blue.

Of late the proportions of ingredients used in preparing ultramarine when soda forms a part have been selected in such a manner, and the heating so conducted, that ultramarine is at once produced.

Uses.—Next to indigo, ultramarine is undoubtedly the most generally used blue pigment. It is used for painting lime-washed walls, plaster of Paris, cement and stucco work, for preparing carpets and paper, in calico printing, etc. Since ultramarine is not in itself adhesive for the above purposes, it requires to be mixed with some substance of an adhesive nature; such as glue, which is used in preparing coloured paper, while for calico printing albumen is used.

Considerable quantities of ultramarine are used for blueing such substances as exhibit or have a tendency to exhibit a brownish or yellowish colour, the real colour of which, ought, however, to be white; such are linen, starch, sugar, paper, stearine, paraffin, etc.

SODIUM THIOSULPHATE.

FORMULA $Na_2S_2O_3$. MOLECULAR WEIGHT 158.

This salt was formerly called sodium hyposulphite, and is still generally known by that name; but it is quite different in composition and characters from the true hyposulphite.

Characters.—Sodium thiosulphate forms large clear monoclinic crystals, which contain five molecules of water, $Na_2S_2O_3 + 5H_2O = 248$, and are unchangeable in the air. The salt is readily soluble in water, and has a bitter cooling taste. When carefully heated, it melts and gives off its water of crystallisation; when more strongly heated, it decomposes into sodium sulphide and sodium sulphate. The solution cannot be preserved long unaltered, but deposits sulphur. An aqueous solution of sodium thiosulphate treated with a mineral acid gives off thiosulphuric acid, which is quickly decomposed into sulphurous acid and sulphur. The property possessed by an aqueous solution of sodium thiosulphate of dissolving the iodides and chlorides of silver is of use in photography; the salt is readily oxidised by iodine and chlorine in presence of water; the hydrogen of the water unites with these haloid elements to form hydrogen acids, and the liberated oxygen combines with the thiosulphuric acid.

Preparation.—Sodium thiosulphate is formed by boiling a solution of sodium sulphite with sulphur, according to the following equation:

$$Na_2SO_3 + S = Na_2S_2O_3;$$

or by the oxidation of sodium pentasulphide, with precipitation of sulphur:

$$Na_2S_5 + O_3 = S_3 + Na_2S_2O_3;$$

or by boiling a solution of sodium hydrate with sulphur, pentasulphide of sodium being formed at the same time:

$$6NaHO + 12S = 2Na_2S_5 + 3H_2O + Na_2S_2O_3;$$

and by exposing the dark coloured solution to the air, the pentasulphide is oxidised and converted into thiosulphate, with separation of sulphur, according to the previous equation.

According to Liebig's method, a solution of sodium carbonate is saturated with sulphurous oxide gas, the product neutralised with sodium carbonate, and the solution of sodium sulphite is mixed with a solution of sodium pentasulphide, prepared by boiling caustic soda with sulphur until saturated. The whole is then filtered, and the filtrate evaporated to crystallisation.

By Walchner's method, a mixture of soda ash with one-third its weight of sulphur is gradually heated to the melting point of sulphur, while constantly stirred. In this way sodium sulphide is formed, which, when heated in the air, takes up oxygen, and is converted into sodium sulphite. The mass upon cooling is lixiviated, and when the clear solution is boiled with sulphur, the sodium sulphite takes up an additional atomic proportion of sulphur and is converted into sodium thiosulphate.

By exposing the waste of the soda manufacture containing calcium oxysulphide to the action of the atmosphere in a moist state, the calcium sulphide is converted into calcium thiosulphate. The oxidised waste is lixiviated, and the liquor boiled with sodium carbonate, by which means calcium carbonate and sodium thiosulphate are formed; the precipitated calcium carbonate is then separated, either by decantation or filtration, and the solution evaporated to crystallisation.

By Kopp's method, soda waste is mixed with 10 or 15 per cent. of sulphur and the mixture is boiled in an iron boiler with from 12 to 15 times its weight of water. Calcium sulphide and thiosulphate are thus formed. The whole liquor is then transferred to close vessels provided with agitators, and sulphurous oxide, produced by burning sulphur, is passed in until the mixture has an acid reaction. This liquor is then drawn off, neutralised with sodium carbonate, allowed to settle, and decanted. The calcium thiosulphate contained in this liquor is converted into the corresponding sodium salt by means of sodium carbonate or sulphate.

Sodium thiosulphate may be obtained in like manner, from the lime used in purifying illuminating gas, which contains calcium thiosulphate, as well as some calcium sulphide.

Uses.—Sodium thiosulphate is employed to a large extent as antichlor in paper manufactories, for removing the last traces of chlorine employed in bleaching the rags. Large quantities of sodium thiosulphate are also used for photographic purposes. Its employment in this branch of industry is due to its capability of dissolving those

parts of photographic negatives that have not been acted upon by light. It is further used in the preparation of silvering and gilding solutions; for extracting silver chloride from silver ores, in the preparation of aniline green, and in cotton printing, etc.

SODIUM SULPHATE.

FORMULA Na_2SO_4. MOLECULAR WEIGHT 142.

History.—This substance was discovered and described in 1658 by Glauber, who prepared it from the residues left in the preparation of hydrochloric acid by the action of sulphuric acid upon common salt. Glauber termed it *sal mirabile*, and subsequently chemists gave it the name *sal mirabile Glauberi*, whence its present designation of Glauber's salt. The first preparation of this salt on a large scale was at Friedrichshall, whence in 1767 it found its way into the market.

Occurrence.—Sodium sulphate occurs in the water of a number of saline springs. The water of several inland seas, as well as sea water itself, also contains sodium sulphate, which is found in the mother liquor obtained in the extraction of common salt from these sources. The water of the lakes of the Araxes plain yields an efflorescence consisting of sodium sulphate, chloride, and carbonate. The salt forms a crust at the edges of the lakes, and when detached it floats upon the surface of the water.

Pure anhydrous sodium sulphate occurs naturally as the mineral thenardite, and in a hydrated condition as mirabilite, while Glauberite is a double compound of sodium sulphate and calcium sulphate. Blodite is a double compound of magnesium sulphate and sodium sulphate. Large quantities of hydrated sodium sulphate are found, together with gypsum and clay, in the valley of the Ebro, in Spain.

Composition.—In the crystallised condition this salt contains 55·9 per cent. of water, and its composition is represented by the formula $Na_2SO_4 10H_2O$.

Characters.—Sodium sulphate crystallises from aqueous solutions at ordinary temperature in well-formed colourless prisms, which effloresce on exposure to the air by giving off their water of crystallisation, becoming first of all opaque and finally falling to powder. 100 parts of water at 0° dissolve 12 parts of crystallised sodium sulphate, at 25° 100 parts, at 33° 322 parts, at 40° 291 parts, at 50° only 262 parts. It will be seen from this that, unlike the generality of salts, the solubility of Glauber's salt in water does not increase with the temperature of the water, but that its maximum solubility is at a temperature of 33°, the solubility then decreasing with rise of temperature. A solution of Glauber's salt saturated at 33° therefore deposits some of the salt in the solid state upon raising the temperature of the solution.

Preparation.—Sodium sulphate is obtained as a by-product in a number of chemical operations, but it is chiefly in the manufacture of sodium carbonate that this salt is produced upon a large scale by heating sodium chloride with sulphuric acid, this operation constituting the first step in the conversion of sodium chloride into sodium carbonate or ordinary soda; the product thus obtained is termed salt cake.

From Common Salt and Sulphuric Acid.—This method is in principle the same as that employed by the discoverer Glauber. The action of sulphuric acid upon sodium chloride to form Glauber's salt may be represented as taking place in two stages, the first stage consisting in the formation of acid sodium sulphate according to the equation:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

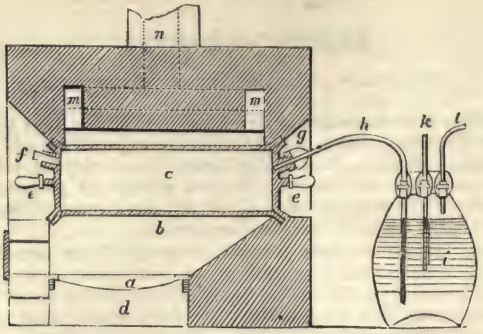
The acid sodium sulphate at a higher temperature then acts upon a further molecule of sodium chloride forming sodium sulphate and hydrochloric acid, thus:

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

An apparatus for the preparation of sodium sulphate in cylinders is shown by figs. 138 and 139. Each furnace, of which from 5 to 25 and more are placed side by side, contains from 2 to 4 retorts (*c c*) of cast iron, each retort being 5½ feet in length and 2¼ feet in width, the retorts being heated by a furnace (*b*). The retorts are built into an arched chamber of fire bricks, and are heated on all sides by the hot air from the fire. The hot air and flame, after being reflected from the arch, pass through the flues (*m*) and (*m*) into the common flue (*m m*), whence they escape into the chimney (*n*). The cast-iron cylinders are closed at both ends with a lid (*c*), luted on by a luting of clay. The interior of each retort is connected with the absorption vessels by means of the stoneware adapter (*h*) fitting air-tight into the retort, and secured by a luting of clay. The other extremity of the adapter passes into the tubulus of a carboy (*i*), which in its turn communicates by means of the tube (*l*) with a series of carboys con-

nected by means of similar tubes, and arranged in rows in connection with one another. The gases escaping from the last row pass through a tube into the common chimney.

Fig. 138.



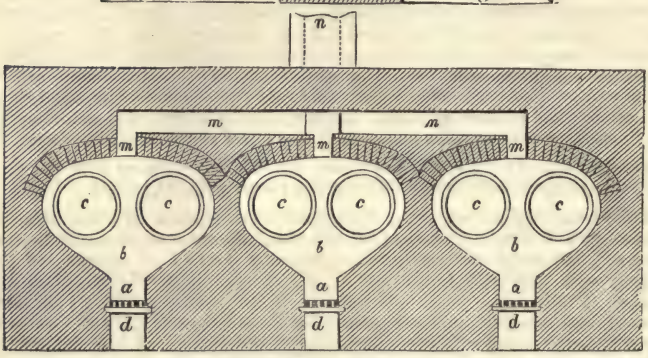


Fig. 139.

The opening (*f*) in the posterior lid of the retort (fig. 138) is for admitting a leaden funnel, the opening being closed during the process with a plug.

Each cylinder receives a charge of about 3½ cwt. of common salt, and then the lid is luted on, and 2½ cwts. of sulphuric acid of sp. gr. 1·727 poured in through the opening (*f*). The funnel is then removed and the opening closed with a plug. The cylinders are heated at first gently, the heat being gradually increased towards the end of the process. The hydrochloric acid evolved passes first of all into the carboy (*i*), which is empty, and serves to retain mechanical impurities carried over with the stream of gas. The hydrochloric acid gas thus purified passes into the carboys of the second row, which are about half filled with water; from thence into those of the third row, the non-absorbed gas escaping finally into the chimney.

The carboys are connected with one another in the way shown in fig. 140. Into the tubulatures of the carboys (A B) are fitted the wide connecting tubes (C D). Through a funnel (G H) water is poured into the carboys; the lower extremity of the funnel dipping beneath the water in the carboy. Caoutchouc tubes (E E′ and F F′) connect the lower part of the carboys with one another. Water is poured in through the funnel (G H), and passes through (E E′) into the second carboy (B), and from thence through (F F′) into the third carboy, and so on until the whole row of carboys has been passed. The hydrochloric acid gas is introduced at the other end of the row of carboys; passes therefore in the direction from D to B, from thence through C to A etc., and during its passage it comes into contact with water of a less degree of saturation, while the water on its passage, coming into contact with vapour of hydrochloric acid of continually increasing strength, becomes saturated more and more.

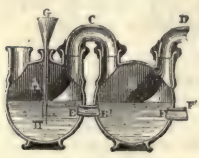


Fig. 140.

Each cylinder yields on an average 440 to 460 lbs. of aqueous hydrochloric acid of sp. gr. 1·160 to 1·170. When the operation is over the saturated solution of hydrochloric acid is let off through the cocks at the bottom of the carboys, and where

the above method is not adopted, the empty carboys of the first row are filled with the partly saturated acid of the following rows.

The residue left in the retorts at the end of the operation, after the hydrochloric acid has all been distilled off, consists of a hard compact mass of sodium sulphate, of about 400 lbs. in weight. This residue is drawn out and the retorts recharged anew in the manner above described.

The materials used in the production of sodium sulphate for the manufacture of soda are the same as those already described, and the only difference is that the operation is conducted in reverberatory furnaces.

In the oldest forms of furnaces in which the action of sulphuric acid upon common salt was effected, the mixture was heated by passing hot air and gas from the furnace directly over it. The reaction between sulphuric acid and sodium chloride was thus very thorough, but it was on the one hand difficult to secure a complete condensation of the hydrochloric acid gas which escaped with the fire gas, and on the other hand the solution of hydrochloric acid obtained was not of the strength required for the manufacture of chlorine, etc. For this reason the ordinary reverberatory furnace ceased to be used in the preparation of sodium sulphate and the reaction of sulphuric acid upon common salt is now carried out in two distinct stages. The first stage consists in preparing acid sodium sulphate in vessels heated from outside, so that the hydrochloric acid escapes unmixed with fire gas. The second stage consists in the preparation of neutral sodium sulphate or Glauber's salt by heating the mixture of acid sodium sulphate and undecomposed salt from the former operation in reverberatory furnaces; this operation is termed roasting the salt cake; the hydrochloric acid thus evolved with the fire gases is condensed either in a series of carboys or some other suitable arrangement to a dilute aqueous solution.

A furnace of the latter kind is represented by figs. 141 and 142. A is the fireplace, B the reverberatory furnace, *d d d' d'* are flues. The latter pass under the leaden pan (E) supported upon an abutment of fire bricks. The fire gas mixed with the hydrochloric acid gas produced in the roasting furnace, after having been made to circulate several times underneath the leaden pan (E), escapes at both ends through the outlets (*d''' d'''*, fig. 142) into a row of carboys (*i'' i''*), where the hydrochloric acid is condensed. Two earthenware tubes (*g g*) having an outlet in the chamber containing the leaden pan (E), terminate respectively in two rows of carboys (*h h'*). A furnace 13 feet in length and 5 feet wide requires for the condensation of the hydrochloric acid from 72 to 78 carboys in the first two rows (*i'' i''*) and from 40 to 50 carboys in the last two rows (*h h'*), each carboy having a capacity of about 44 gallons. K is an aperture for admitting the common salt; (*e*) a damper for placing the roasting space in communication with the pan space.

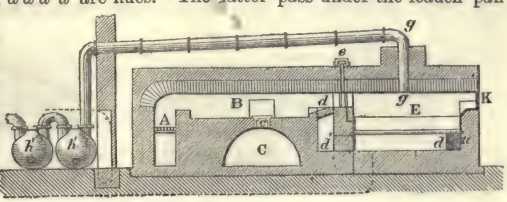


Fig. 141.

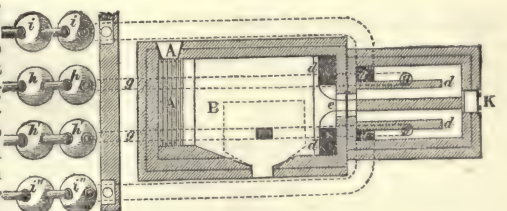


Fig. 142.

The leaden pan (E) is charged with common salt in the following way:—First of all salt is thrown in at K and spread over the pan; then sulphuric acid, generally a chamber acid of sp. gr. 1·520 to 1·550, is poured in through a funnel tube bent at right angles; K is then shut and luted. Hot air is then passed under E, the escaping vapour of hydrochloric acid being passed through *g g* into the carboys (*h h'*).

The complete formation of acid sodium sulphate in the leaden pan is noticed by the liquid mass assuming a stiff consistency; the damper (*e*) is then drawn up and the acid sodium sulphate thrown through *e'* by the aid of a suitable spatula into the roasting chamber (B). The damper (*e*) is then let down and the leaden pan again charged with common salt and sulphuric acid, while at the same time the acid sodium sulphate and unchanged sodium chloride is strongly heated in the roasting furnace to form neutral sodium sulphate, the hydrochloric acid evolved passing, together with the fire gas, underneath E, then through *d d* into the condensers (*i'' i''*). The mass

in the calcining chambers is continually stirred during the operation so as to secure an equal roasting. When the operation is over, the Glauber's salt is in the state of a coarse-grained powder.

The condensation of the hydrochloric acid gas escaping from the reverberatory furnace is difficult, for the reason that it is mixed with the fire gas, which is in itself non-condensible and consequently carries off mechanically large quantities of hydrochloric acid. A further requirement of this method is a tall chimney to carry off the non-condensed vapour of hydrochloric acid gas, so as to prevent its causing a nuisance to the immediate vicinity.

The condensing system described on p. 250 (fig. 140), in which the lower parts of the condensing carboys are connected with caoutchouc tubes, and where it is only necessary to pour water into the last carboy of a whole row, is here too the most suitable system to adopt.

As soon as the decomposition in the calcining or reverberatory furnace is complete, the iron lid (*c*) which had served during the operation to cover the arched vault (C) is removed, the sodium sulphate raked out into the vault, and the furnace recharged.

Alterations in the Construction of the Furnaces.—The chief propositions made as to improvements in sodium sulphate furnaces aim at getting rid of the reverberatory furnace used for heating the mixture of acid sodium sulphate and common salt as it comes from the lead pan in the first stage of the process. For not only does a great loss ensue by the impossibility of effectually absorbing vapour of hydrochloric acid mixed with fire gas, but further it is very difficult, if not impossible, to prevent the large quantities of hydrochloric acid which escape from injuring the surrounding neighbourhood.

Figs. 143, 144 and 145 represent a furnace where the sulphate is calcined in a muffle. Figs. 143 and 144 show the furnace in section, fig. 145 the ground plan as high as the grate. A A are two fireplaces with grate 2 feet long and 1½ feet wide.

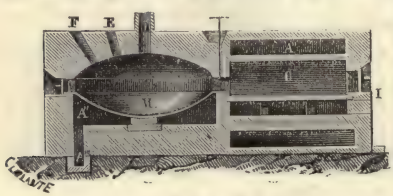


FIG. 143.

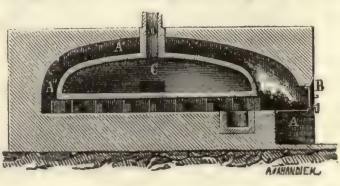


FIG. 144.

The flame plays round the muffle in the direction from A' to A'' and then passes underneath the leaden pan (M), and from thence through a flue (A''') underneath leaden pans for concentrating chamber acid. The muffle (C) is made of single plates of fire clay cemented together perfectly air tight. The bottom of the muffle is 13 feet long, and about 8¼ feet wide. The arch above the muffle is also built of fire brick. A couple of tubes (D D) serve to conduct the hydrochloric acid developed in the muffle and pan space into the condensing apparatus. A'' is a damper, by lifting which the muffle (C) and the pan (M) are placed in communication. The pan (M) has a round shape with a diameter of 10 feet, and stands in a brickwork chamber. The opening (E) communicates with the hopper of the salt reservoir, and serves for admitting salt into the muffle ; a similar opening (F) serves to admit the sulphuric acid. J is an opening admitting of the mass in M being stirred for an hour, after which it is brought into the muffle. I is an opening communicating with the muffle (C). The operation is conducted in a way similar to that described in the case of the previously mentioned furnace. Each charge consists of about 12 cwts. of salt, and 13 cwts. of sulphuric acid of sp. gr. 1·652. Calculating 12 charges to every 24 hours, 144 cwts. of common salt would be worked up by a single furnace every 24 hours, or 36 tons would be worked up in this time in a factory provided with six sulphate furnaces, and with five of them working.

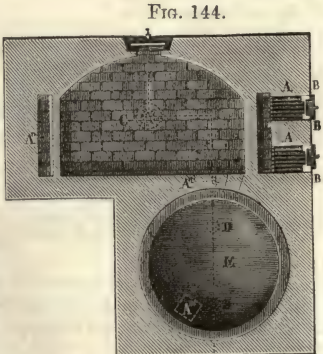


FIG. 145.

In this country the leaden pans are replaced by cast-iron pans weighing as much as 5 tons. They are sometimes not set in arched brickwork, the latter being re-

placed by domed covers of cast iron. The fire gases from the roasting furnace are not used for heating the pans, which are heated by a separate fire.

Modifications in the Condensing Apparatus.—The various forms of condensing bottles have been already mentioned. In places where it was found necessary to absorb the last traces of hydrochloric acid, various absorbents have been propcsed in the place of water. Kuhlmann fills the last carboy with pieces of coke over which a stream of milk of lime is made to trickle; the large surface of alkaline liquid absorbs the hydrochloric acid completely. In order to obtain barium chloride as a by-product he replaces the milk of lime by witherite in a fine state of division.

Condensing Towers, Coke Towers.—In very large works, especially in this country, the condensing carboys are replaced by towers having an arrangement similar to the Gay-Lussac's coke towers described on p. 124. The towers, of which a couple are placed together communicating with one another above, are built of sandstone saturated with tar, and are filled either with coke, broken pieces of earthenware, or flints, over which a stream of cold water is kept constantly flowing. The acid vapour enters at the lower part of one of the towers, passing through a perforated

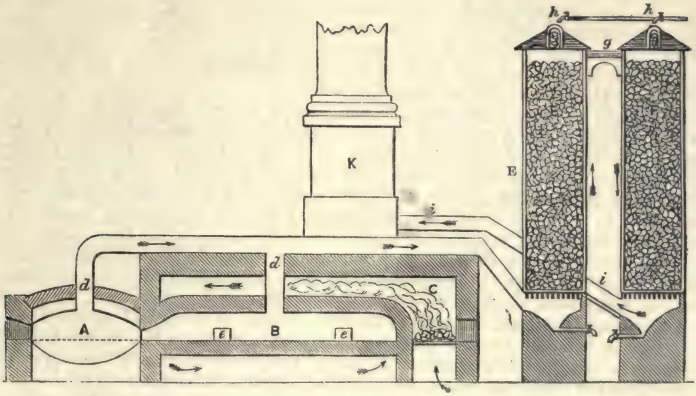


Fig. 146.

vault upon which the pieces of coke, etc. rest, and then through the moistened coke into the upper part of the next tower, passing downwards through it into a chimney. The aqueous hydrochloric acid thus formed is let off through pipes placed at the lowest part of the towers. The acid of the first tower is of course more concentrated than that of the second one. An arrangement of this kind is represented by fig. 146.

Instead of two towers, in some places a single tower is employed, divided by a partition into two chambers. The acid vapour passes, as in the other case, upwards through the first chamber and downwards through the second, escaping from beneath the latter into the chimney.

Sodium Sulphate from other sources.—Considerable quantities of this salt are obtained from the mother liquors of brine springs, sea water, and kelp, and as a by-product in the manufacture of potash salts from the saline deposits at Stassfurt.

The preparation of sodium sulphate from the mother liquor of saline springs, or sea water, depends upon the fact that the magnesium sulphate contained in the mother liquor of brine, and of sea water, reacts upon the sodium chloride at a low temperature, forming sodium sulphate and magnesium chloride, the former separating in the crystalline condition, while magnesium chloride remains in solution. (*Vide* p. 200.)

The scales found in the pans in which concentrated brine has been boiled down are scraped off and lixiviated with water, which dissolves the sodium sulphate, leaving the gypsum undissolved. The liquor thus obtained is used for lixiviating fresh pan scales until a liquor has been obtained having a spec. grav. of 1·197 or 1·206. This is either decanted or filtered from the gypsum and the sodium sulphate crystallised out in the winter season.

Sodium sulphate is obtained from the residues of the Stassfurt potash works on a large scale at the works of Messrs. Ziervogel and Tuchen at Stassfurt. The residues from the lixiviation of raw carnallite, consisting chiefly of common salt and kieserite (magnesium sulphate), are exposed to the action of the air for several weeks. In course of time the insoluble kieserite is converted into soluble magnesium sulphate;

the mass is then lixiviated in large tanks, and the solution exposed in shallow wooden basins to a low temperature. A crystallisation of sodium sulphate is thus obtained, which, after the mother liquor has been drawn off, is collected and dried. The conversion of hydrated sodium sulphate into the anhydrous condition is effected at the above works by heating it over a water bath with constant stirring.

In preparing sodium sulphate from common salt and ammonium sulphate, a solution of common salt, having a spec. grav. of 1·160, is mixed with an equivalent quantity of ammonium sulphate, and the mixture heated to the boiling point. A mutual decomposition takes place, sodium sulphate and ammonium chloride (sal ammoniac) being formed, the former separating in the solid state. Upon evaporating the mother liquor a further crop of sodium sulphate is obtained. The mother liquor is finally drawn off into suitable vessels, and yields upon cooling crystals of sal ammoniac, which are either simply dried and sent into the market, or are first of all submitted to a process of sublimation.

When a mixture of ferrous sulphate and sodium chloride is heated to redness in a current of air, there are formed sodium sulphate, ferric oxide, and free chlorine. The mother liquor from the preparation of ferrous sulphate, or mine water containing this salt, may be employed for the purpose, common salt being dissolved in the solution, the mixture evaporated to dryness, and the residue heated to redness in a current of air. The sodium sulphate is then extracted with water. Another plan consists in freezing out sodium sulphate from a solution containing common salt and ferrous sulphate. This operation is performed in winter.

Tilghman prepares Glauber's salt from gypsum and common salt by melting the two salts, and passing a stream of superheated steam over the melted mass; sodium sulphate is thus formed and hydrochloric acid, which escapes. Anthon prepares a mixture of equal parts salt, gypsum, and calcined magnesia, stirs the mixture up with a quantity of water equal to double its weight, and passes carbonic acid into the mixture. In this way magnesium carbonate is formed, which with gypsum yields calcium carbonate and magnesium sulphate, and by evaporating the solution of this salt, mixed with sodium chloride, they yield magnesium chloride, and sodium sulphate which crystallises out. Other methods of preparing sodium sulphate, consisting in roasting magnesium sulphate, copper vitriol or zinc vitriol, pyrites, etc., with common salt, have been proposed, but none of them have received industrial application.

There is, however, another process recently introduced by Mr. Hargreaves, which promises to bring about a considerable change in the manufacture of sodium sulphate. This consists in subjecting salt to the action of a mixture of sulphurous oxide, obtained by burning pyrites, with atmospheric air and steam, so as to convert the sulphurous oxide into sulphuric acid, and the sodium chloride into sulphate, with liberation of hydrochloric acid; the reaction taking place is represented by the following equation:

$$2NaCl + H_2O + SO_2 + O = Na_2SO_4 + 2HCl.$$

For the purpose of preparing sodium sulphate in this way, several cylinders of cast iron, arranged so that they can be heated externally, are filled with salt in a dry porous condition, and when heated to a temperature of about 426°, a mixture of sulphurous oxide, air, and steam is passed in at the top of one of the cylinders, at the bottom of which is a pipe communicating with the top of the next cylinder. After a time, when the salt in the first cylinder is wholly converted into sulphate, the gas is passed into the second cylinder, and after removing the sulphate from the first one, it is connected with the last cylinder, and so on through the entire series.

Purification.—Sodium sulphate is purified by dissolving the raw salt in boiling water, allowing the solution to settle, decanting it off from the sediment, and crystallising in wooden troughs lined with lead. As soon as the temperature of the solution has sunk a few degrees below 33°, crystallisation commences, and further cooling produces large well-formed, transparent prisms of sodium sulphate.

When it is desired to obtain sodium sulphate with the appearance of Epsom salts, the solution is stirred during the cooling process, so that no large crystals can form.

Uses.—The chief use made of Glauber's salt or sodium sulphate is in the preparation of soda by Leblanc's method. Besides this, large quantities of the salt are used in glass manufacture. Another important application of sodium sulphate is in the preparation of ultramarine.

Sodium sulphate is further used for separating calcium, as sulphate, from various mother liquors, such as those of saltpetre, which contains calcium chloride, for preparing sodium acetate by decomposing calcium acetate, obtained in the saturation of raw wood vinegar. Sodium sulphate is sometimes heated to redness with charcoal, so as to obtain sodium sulphide, which is used for odourless sulphur baths. Finally, it is used in dye works, and for the production of freezing mixtures. An excellent

freezing mixture is obtained by mixing 4 parts of crystallised sodium sulphate with 3 parts of sulphuric acid of sp. gr. 1·360, or 8 parts of powdered sodium sulphate with 5 parts of fuming hydrochloric acid.

SODIUM CARBONATE.

FORMULA Na_2CO_3. MOLECULAR WEIGHT 106.

History.—Mention is made in the Old Testament of a substance called neter which possessed the property of effervescing with vinegar; it was a natural product obtained from certain lakes in Egypt, and was used for cleaning purposes in the same way as wood ashes, and it cannot well have been anything else than soda. It was this substance, and not nitre, as was at one time supposed, that was mentioned by ancient Greek and Latin authors under the names *νίτρον* and *nitrum*, as representing the Egyptian name. The terms natron and soda were first applied to this substance in the fifteenth century. For a long time no distinction was made between potash and soda; and even as late as the last century both substances were held to be identical, or at most only modifications of one and the same substance. It was not until Stahl in 1702, and Duhamel in 1736, had shown that common salt contained a base differing from ordinary potash, that soda and potash were proved, chiefly by Marggraff's investigations, to be different substances.

Up to the beginning of the present century soda was obtained exclusively from the ashes of land and marine plants; but as early as the middle of the last century attempts had been made to prepare soda from common salt. In 1782, according to Kirwan, attempts to obtain soda from common salt were made in England by applying the reaction discovered by Scheele, and decomposing salt with litharge, filtering the solution, and exposing it to the air for absorption of carbonic acid. This attempt, as well as a number of others of a similar kind, did not attain the desired result, owing to the fact that soda obtained from the ashes of plants was cheaper than that produced by any of those methods.

It was not until a decree came into force in France prohibiting the importation of soda into that country, that the method of preparing soda from common salt devised by Leblanc, Dizé, and Shée was adopted. This method is now commonly employed.

Occurrence.—Sodium carbonate occurs naturally under various conditions. In the solid form it occurs as an efflorescence as well as in some minerals; in a state of solution it is present in many kinds of mineral water, as at Carlsbad, Aix la Chapelle, Vichy, etc. Sodium sesquicarbonate is found in considerable quantities in the water of the soda lakes of Egypt, Central Africa, South America, in the vicinity of the Caspian Sea, in Arabia, Hungary, etc. From some of these sources soda is still prepared industrially. There are two kinds of natural soda, known as Trona and Urao.

Trona is obtained from Egypt, and it consists essentially of a compound represented by the formula $Na_4C_3O_8 + 4H_2O$, together with some admixtures of sodium sulphate, sodium chloride, and earthy impurities. The amount of anhydrous sodium sesquicarbonate is about 60 or 70 per cent. It occurs as an incrustation formed by the evaporation of the water in pools or lakes, and sometimes separates from the water in masses which float on the surface.

Urao is obtained from the water of Lake La Lagunilla, in Columbia, and it also contains sodium sesquicarbonate. During the hot season the urao is deposited from the water of the lake, in consequence of evaporation, and is collected. It is a purer material than trona, but the quantity produced is less.

Native soda is also obtained from some Hungarian lakes, but the annual amount now produced is small, although the production was formerly more considerable. The Hungarian soda contains less sodium sesquicarbonate than trona or urao.

The ashes of some marine plants, as well as the ashes of plants growing on the sea coast, often contain, besides various other salts, a quantity of sodium carbonate. The manner of preparing kelp or varec has been already treated of, on p. 194. The composition of the ash of soda plants varies according to the kind of plant from which the ash is obtained, and according to the locality where the plants grow. The ash of such plants under the name of barilla formerly constituted one of the chief sources of soda, and this alkali was also obtained to some extent from kelp.

Barilla comes chiefly from Alicante, Malaga, and Carthagena; it is the best kind of soda obtained from soda plants, and contains from 14 to 30 per cent. of sodium carbonate, together with sodium and potassium chlorides and potassium sulphate.

Blanquette comes from the coast between Aigues-Mortes and Frontignan, and contains from 8 to 10 per cent. of sodium carbonate. Salicor comes from Narbonne, and contains from 14 to 15 per cent. of sodium carbonate.

The amount of sodium carbonate in kelp varies between 2½ and 5 per cent.

Characters.—Sodium carbonate occurs in the market as calcined soda, or soda ash, either entirely anhydrous or containing but little water, and as crystals, which contain 10 molecules of water of crystallisation. Crystallised soda forms large colourless crystals, belonging to the klinorhombic system. Exposed to the atmosphere the crystals become opaque, owing to loss of water of crystallisation, and at last crumble to a fine powder. Crystallised soda, heated to 34°, melts in its water of crystallisation; subjected to a still stronger heat, after parting with nine-tenths of its water of crystallisation, it again becomes solid, then gives off the remaining water of crystallisation, at last melting, and upon cooling it solidifies to a crystalline mass.

Sodium carbonate resembles Glauber's salt (sodium sulphate) in respect to its solubility in water, and deviates from the general rule, inasmuch as the solubility of the salt does not increase with the rise of temperature beyond a certain point. The greatest solubility is at a temperature of 36°; a further addition of heat to a solution of sodium carbonate saturated at this temperature causes a deposition of some of the salt in the solid state. The following table gives the solubility of anhydrous sodium carbonate in 100 parts of water at different temperatures:

Temp.	Anhy. Sod. Carb.	Temp.	Anhy. Sod. Carb.
0°	6·97	25°	28·50
10°	12·06	30°	37·24
15°	16·20	38°	51·67
20°	21·71	104°	45·47

When a hot solution of sodium carbonate is allowed to cool without disturbance, it becomes supersaturated—*i.e.* the liquid retains more salt dissolved than corresponds to the low temperature of the solution. Upon agitating a solution of the salt in this state, the excess of salt held in solution is suddenly separated in crystals containing often 7 instead of 10 molecules of water of crystallisation.

The percentage of anhydrous soda contained in aqueous solutions of the salt can be ascertained from their specific gravity, as given in the following table by Gerlach, constructed for a temperature of 15°:

Spec. Grav.	Percentage of Sodium Carbonate	Spec. Grav.	Percentage of Sodium Carbonate
1·0105	1	1·0843	8
1·0210	2	1·0950	9
1·0315	3	1·1057	10
1·0420	4	1·1165	11
1·0525	5	1·1274	12
1·0631	6	1·1384	13
1·0737	7	1·1495	14

Preparation.—The method by which sodium carbonate or soda is now chiefly prepared dates from the year 1794, and was introduced by Leblanc; it involves three distinct operations:

1. The conversion of sodium chloride, or common salt, into sodium sulphate, or salt cake, by means of sulphuric acid.
2. The conversion of sodium sulphate into sodium carbonate, by heating salt cake with calcium carbonate and carbon.
3. The extraction of sodium carbonate from the black ash obtained by the last operation.

Several other methods of preparing sodium carbonate have been suggested at various times, but none of them have yet superseded that of Leblanc.

From Sodium Sulphate.—The production of sodium carbonate in this way constitutes the second stage of the modern process of soda manufacture. Sodium sulphate prepared from common salt by Leblanc's method, as already described on p. 251, is converted into carbonate by heating it to redness with carbon and calcium carbonate, and the product thus obtained is termed black ash or ball soda.

The process was formerly supposed to take place in three stages:—

1. Reduction of sodium sulphate to sulphide by the action of charcoal:

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

2. Mutual conversion of sodium sulphide and calcium carbonate at a red heat into sodium carbonate and calcium sulphide:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

3. Combination of calcium sulphide with lime to form insoluble calcium oxysulphide:

$$2CaS + CaO = Ca_3S_2O.$$

Unger considers the process of soda formation from sodium sulphate to be of a more complex nature than that above given. He represents the process as taking place in the following stages:—

1. Conversion of one-third of the sodium sulphate by reaction with calcium carbonate into sodium carbonate and calcium sulphate, without the agency of charcoal:

$$Na_2SO_4 + CaCO_3 = Na_2CO_3 + CaSO_4.$$

2. Reduction of the remaining two-thirds of the sodium sulphate by charcoal to sodium sulphide:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

According to Unger, this reduction is effected not only by the carbon, but also by nascent hydrogen produced by the action of carbon at a red heat upon water, and by the carbonic oxide, produced by the action of carbon upon carbonic acid.

3. Mutual conversion of the sodium sulphide and calcium carbonate at a red heat into sodium carbonate and calcium sulphide:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

4. Formation of calcium oxysulphide by the action of steam upon calcium sulphide, formed either by this reaction, or by the reduction of calcium sulphate by carbon:

$$4CaS + H_2O = Ca_4S_3O + H_2S.$$

5. The sulphuretted hydrogen thus formed combines with caustic soda or sodium carbonate to form sodium sulphide, which yields with calcium carbonate sodium carbonate and calcium sulphide, etc.

Kynaston considers that ball soda does not contain calcium oxysulphide, but only sodium carbonate, calcium sulphide, and lime; and that upon dissolving the fused mass these substances react upon each other in the following way:—

1. The lime and sodium carbonate yield calcium carbonate and caustic soda.

2. The caustic soda and calcium sulphide form sodium sulphide and hydrate of lime.

Kolb likewise questions the formation of calcium oxysulphide in the soda process. According to him the process is as follows:—

1. The sodium sulphate is reduced by carbon at a red heat to sodium sulphide:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

2. Lime is formed by the action of carbon upon calcium carbonate:

$$CaCO_3 + C = CaO + 2CO.$$

3. Sodium sulphide, in contact with excess of lime and carbonic acid, yields soda and sodium sulphide:

$$Na_2S + CaO + CO_2 = Na_2CO_3 + CaS.$$

According to Kolb, the calcium sulphide thus formed is so insoluble in water that it is unnecessary, on account of the insolubility of the material, to assume the presence of calcium oxysulphide.

Sodium thiosulphate is always formed when the melted material has been a long time in contact with atmospheric air, and become disintegrated, the metallic sulphides being thus oxidised to thiosulphates.

The relative proportions in which the ingredients should be taken, as given by Leblanc, are as follows:—

Sodium sulphate	1000 parts
Calcium carbonate	1000 ,,
Carbon	550 ,,

Generally there has been but little deviation from these proportions, as may be seen from the following table given by Scheurer-Kestner, as representing the mixture used at ten different works.

	1	2	3	4	5	6	7	8	9	10
Sodium sulphate	100	100	100	100	100	100	100	100	100	100
Calcium carbonate	107·7	110	103	97·5	115	121	115	93·6	100	90·2
Carbon	73	50	61·7	55·6	35	46·6	68	40·4	40·3	42·1

The sodium sulphate is used in the anhydrous state, and it ought to be as free as possible from sodium chloride, because this salt would render the soda impure. The sodium sulphate ought also to be free from excess of sulphuric acid, and from ferric oxide, which is apt to be produced when the sulphate has been too strongly heated, and would render the fusion of the material more difficult.

The calcium carbonate employed may very conveniently be in the form of chalk, or, where that is not obtainable, tufaceous limestone, muschelkalk, or ordinary limestone may be taken. The chief point is to have the calcium carbonate as pure as possible, and in all cases it is used in the state of a fine powder. Carbon is supplied in the form of coal, with as little silica as possible in the ash, so as to avoid the formation of soluble sodium silicate which would pass into the soda undecomposed, and also of insoluble silicates, containing sodium, which would cause a loss of sodium carbonate. The coal is generally employed in coarse fragments.

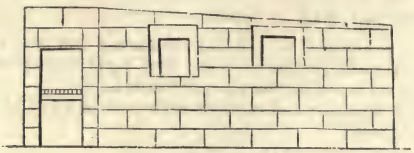


Fig. 147.

The 'balling' furnaces employed for conducting this operation in soda works are reverberatory furnaces, the construction of which is represented by figs. 147 and 148. In most balling furnaces the hearth or bed is divided into two parts, and, as shown in fig. 148, the hearth nearest the fire is lower than the one furthest from it. Sometimes these portions of the hearth are separated from one another by a bridge. In these furnaces, the charge is first placed upon the higher hearth furthest from the fire and is heated by the flame from the lower hearth. After the lapse of about an hour the mass is pushed off the upper hearth on to the lower one where the reaction begins, and it is consequently only necessary to stir the mass upon this part of the hearth. A furnace of this kind with about 100 square feet superficial area, where the united charges of the two hearths amount to 5 cwt., and where charging takes place every hour, yields 6 tons of raw soda per 24 hours. Formerly small furnaces were employed which were succeeded by furnaces of larger dimensions, which have again been replaced by small furnaces, for the reason that the mixture was not equally heated in the larger furnaces.

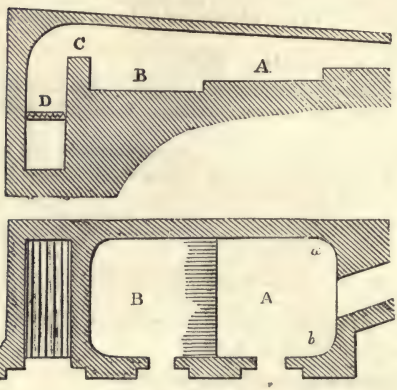


Fig. 148.

A furnace of the kind used on the continent is represented by figs 149 and 150. *a* is the ash hole, *b* fire-place with horizontal grate, *c* fire-bridge separating the fire-place from the hearth (*d d*). The hearth and the arch above it are built of fire brick; the flues (*e e*) conduct the hot air from the furnace, either direct into the chimney (*f*), or into a horizontal flue beneath the hearth, from thence underneath evaporating pans, into the general chimney. The four side doors (*g g g g*), and the door (*h*) opposite the fire-place, serve as working holes through which a workman stirs or withdraws the soda. The stirring operation is assisted by an iron roller (*i i*), before each door, upon which an iron stirrer is laid. The arch is furnished with three openings (*j j j j*), for charging the furnace, but as they affect the solidity of the masonry of the arch, they are often left out, and the charging is then effected with shovels. The other arrangement has, however, this advantage, that the mixture is previously warmed by lying over the furnace vaulting.

The furnace is strongly heated before charging, and the mixture is placed upon the hearth in coarse lumps, the whole being strongly heated until it melts, and then the liquid mass is frequently stirred with the stirrer (A). The termination of the operation is indicated by diminution of the flames of carbonic oxide, which at the beginning of the process cover the surface of the entire mass. The ball soda is then raked out from the furnace with the rake (B) into iron boxes mounted on wheels. The heating is not kept up until the flames of carbonic oxide have entirely ceased, because in that case oxidation would take place, and sodium sulphate would be formed. Too high a tem-

perature must also be avoided, especially towards the end of the operation, since, on the one hand, it would cause considerable loss of soda by volatilisation, and would also have the effect of making the ball soda impure by the decomposition of the fire clay forming the hearth by sodium carbonate and the formation of silicates.

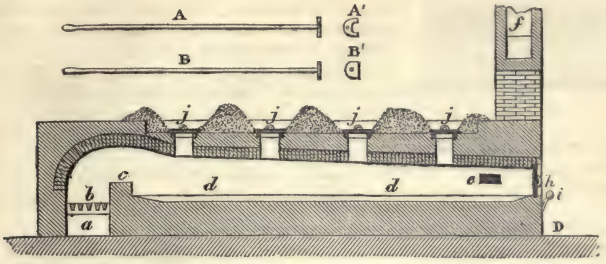


FIG. 149.

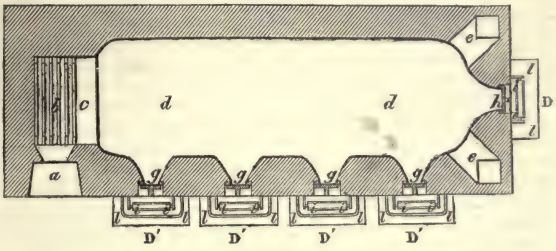


FIG. 150.

Figs. 151, 152 and 153 represent a soda furnace of another construction. A the furnace door, A′ ash pit, A″ grate, B fire bridge; C C hearth of the furnace, which is about

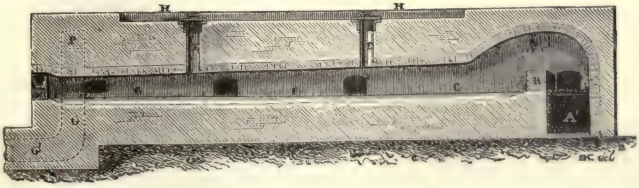


FIG. 151.

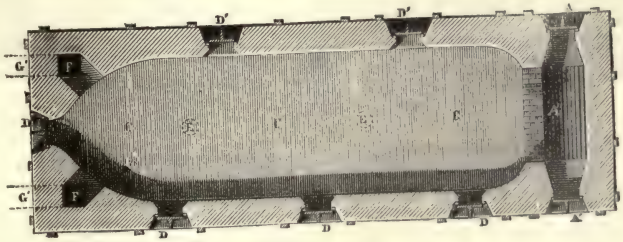


FIG. 152.

5 inches deep. D D D are three side doors; D′D′ two side doors, placed in such a way that each door is opposite the space between each two doors on the opposite side. Their

position enables a stirrer thrust in through one of the doors to reach the soda on the other side. E E are openings in the arch of the furnace, furnished with cast-iron tubes which serve for charging the furnace. F G are flues through which the hot air from the furnace passes into the horizontal flue (G'), and from thence either under pans for evaporating or under the surface for drying common salt. H is a second hearth serving for heating the mixture previous to its admission into the furnace. The charging and mode of working of this furnace are similar to that described in the one previously mentioned. A furnace of this kind yields every 24 hours, during which time six operations are carried out, nearly 9 tons of ball soda of 38 alkalimetrical degrees.

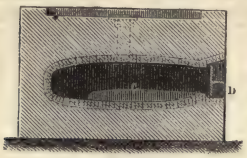


Fig. 153.

Some soda furnaces are built in such way that the hot air from the furnace after passing the second hearth is conducted over pans filled with soda liquor for evaporation.

Another kind of soda furnace is that with rotatory hearth invented by Elliot and Russel, and improved by Stephenson and Williamson, represented by fig. 154. This furnace differs from all former soda furnaces in this respect, that the stirring of the materials by manual labour is dispensed with, the stirring operation being effected by machinery. A is the rotatory hearth, consisting of a cylinder of cast iron lined internally with fire clay. Ribs or rails (B) cast on the cylinder run on the wheels (C), receiving motion from the driving wheel (O), and causing the cylinder to rotate. The heated air of the furnace (D) flows through the opening (E) into the cylinder, and passing through (F), reaches the arched compartment (G), and is carried off by the flue (F) into the chimney. The cylinder is charged by allowing the materials to fall into it through an opening (B') from a small iron truck (J) through the hoppers (H). The cylinder is also emptied through B', for which purpose the cylinder must be so turned that the opening is below. A cylinder of the kind is generally about 13 ft. long and 7 ft. in diameter. In order to charge it, there is first of all thrown in about 3 cwt. of chalk and 1 cwt. of coal or charcoal powder, the cylinder being thus caused to rotate slowly and heated for an hour and a half. The rotation is then stopped, and $2\frac{3}{4}$ cwt. of sodium sulphate and $\frac{3}{4}$ cwt. of charcoal are added, and the cylinder again caused to rotate slowly, the heat being gradually increased, until it is observed that the mass has begun to melt, when a rotation is given to the cylinder of one revolution every three minutes. When the operation is over the melted mass is run out at B' into iron trucks.

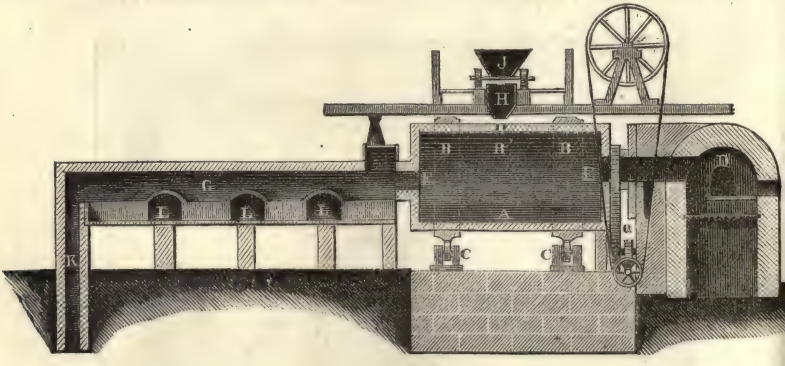


Fig. 154.

The use of these cylindrical furnaces effects a more complete and quicker decomposition of the materials than can be obtained in the other kinds of soda furnaces. At the same time the oxidising action of the atmospheric air is avoided which, in the older forms of furnaces resulted from the access of air through the working holes. Moreover the cylindrical furnaces yield three times as much product, and as the fire bricks of the cylinder do not suffer from raking, as is the case in the hearths of other kinds of furnaces, the cylindrical furnaces are more durable. Wagner states that at the Jarrow chemical works, where formerly only one rotatory soda furnace was employed, several of them have recently been erected, which speaks well for their utility.

In former times when no extensive use was made of the hydrochloric acid evolved

in the preparation of sodium sulphate from common salt, soda and sodium sulphate furnaces were connected with one another, and this is the case even at the present day in some places. Figs. 155 and 156 represent the construction of a furnace of the kind.

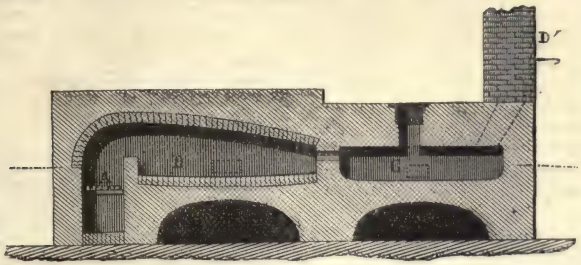


Fig. 155.

B is an ordinary soda furnace, C the sulphate furnace. The hot air from the furnace (A) flows over the fire bridge into the chamber (B), causing the raw soda in it to melt, and it then passes into the sulphate chamber (C) and through the flues (D D) into the chimney (D′). The sulphate which is obtained from (C) in the calcined state is drawn out, mixed with charcoal and calcined carbonate, and brought into the soda furnace (B).

The hearth of the soda furnace (B) is 10 ft. 8 in. long, and $8\frac{3}{4}$ ft. wide; the

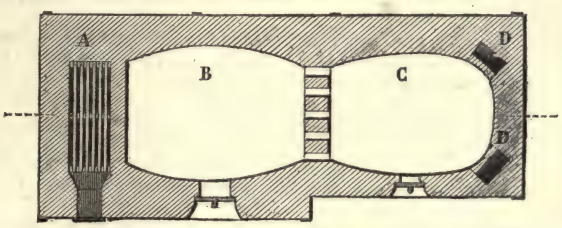


Fig. 156.

hearth of the sulphate furnace (C) is 9 ft. 6 in. long and 8 ft. 6 in. wide. The sulphate furnace is charged three times within the space of 24 hours, making an entire charge of $31\frac{1}{2}$ cwt. of common salt and 40 cwt. of sulphuric acid, of specific gravity 1·535, the produce being about $37\frac{1}{2}$ cwt. of sodium sulphate. The latter quantity is operated upon in the soda furnace in twelve operations with about 40 cwt. of calcium carbonate and 22 cwt. of coal or charcoal, the amount of ball soda produced being about 55 cwt. of 38–40 alkalimetrical degrees.

Combined soda and sulphate furnaces have been constructed with three divisions, of which the one furthest from the fire is used for decomposing the salt with sulphuric acid, the next one for calcining the sulphate, the last or partition nearest the fire being the soda furnace.

Lixiviation and Purification of Ball Soda.—The composition of ball soda varies considerably, and it depends upon the proportions of the raw materials taken, and the way in which the process of soda-making is carried out.

Apart from accidental admixtures, ball soda has, according to Wagner, the following composition:—

Sodium carbonate	45
Calcium sulphide	30
Caustic lime	10
Calcium carbonate	5
Foreign substance	10

The percentage of sodium carbonate in ball soda is, at any rate in most cases, less than 45 per cent.; but it fluctuates more than is indicated by the analyses, and is sometimes less than 30 per cent.

The following table gives the results of three analyses by Stohmann of ball soda from the Jarrow soda works :—

	Soda prepared in an ordinary furnace		Soda prepared in cylindrical furnace
Sodium carbonate	44·41	38·45	43·27
„ hydrated oxide	—	3·17	—
„ sulphate	1·54	1·54	1·06
„ chloride	1·42	1·75	1·48
Calcium carbonate	3·20	—	7·52
„ oxysulphide	38·98	36·91	25·48
„ sulphide	—	—	9·38
Lime	0·33	0·61	—
Magnesia	0·10	0·51	0·19
Alumina	0·79	—	0·72
Ferric oxide	1·75	2·40	1·48
Silica (soluble)	0·89	1·36	1·74
Sand	2·20	1·16	2·66
Carbon	5·32	5·43	5·28
Water	6·71	—	—
	100·90	100·00	100·17

The object of the lixiviation of ball soda is the separation of the soluble constituents, chiefly sodium carbonate, from the insoluble constituents, such as calcium sulphide or oxysulphide, lime, carbon, etc.

If the melted material, when removed from the furnace, were to be allowed to cool in the air, a number of changes would take place, causing a loss of soda. It has been proved, for instance, that by contact with atmospheric air the calcium sulphide is rapidly oxidised to sulphate, which, in lixiviating the ball soda, reacts upon part of the sodium carbonate, forming calcium carbonate and sodium sulphate. A further loss of sodium carbonate is sustained, even by allowing the cold material to lie exposed to moist air, a part of the calcium sulphide being oxidised to thiosulphate, which reacts upon sodium carbonate, forming calcium carbonate and sodium thiosulphate.

The only advantageous process of oxidation is the oxidation of sodium sulphide to thiosulphate. But, besides this, exposure to the action of atmospheric air has a favourable effect in causing disintegration of the mass, since the caustic lime absorbs water, and is thus converted into hydrate of lime—a process which is very favourable to the following operation of lixiviation. However, since calcium sulphide oxidises in contact with moist air, forming calcium thiosulphate, which causes loss of soda by forming sodium thiosulphate, the material should not be exposed to the action of the air for a longer time than is necessary for its disintegration. According to the condition of the material and the atmospheric moisture, this requires from 3 to 6 days.

In addition to the precautions that are requisite as above mentioned in order to prevent loss of sodium carbonate as a result of the oxidation of the calcium sulphide in the ball soda, it is also necessary to prevent the access of air to the ball soda while it is at a high temperature, for in that case calcium sulphate would be formed by oxidation, and in the subsequent lixiviation of the ball soda a proportionate quantity of sodium carbonate would be converted by reaction with it into sodium sulphate. On this account it is customary to draw the ball soda from the furnace into sheet-iron boxes furnished with close-fitting covers and mounted on wheels.

Breaking up of the Ball Soda.—This operation is sometimes effected by allowing the material to disintegrate in contact with moist air, or by treating it with steam in a closed chamber. However, these methods are not suitable for large quantities, and in such case the ball soda is broken up into pieces about the size of the hand, and then ground to a coarse powder between mill-stones, or else broken into pieces about the size of small nuts, between grooved or spiked rollers. Another method consists in stirring the melted black ash as it comes from the furnace into the crushed fragments of a previous charge.

Lixiviation.—In this operation the soluble substances must be dissolved out from the crude soda with as little water as possible. The use of too much water would involve unnecessary expenditure of time and fuel in the subsequent evaporation of the

solution. On this account, therefore, the liquid is repeatedly brought into contact with fresh portions of material, so as to make it fully saturated.

Hard and difficultly soluble ball soda requires to be lixiviated with hot water; but the temperature should not exceed 35°, otherwise calcium sulphide reacts upon sodium carbonate to form sodium sulphide and calcium carbonate

A lixiviating apparatus is represented by fig. 157. It consists usually of from 12 to 14 rectangular iron tanks (A, B, C, D, E), placed in steps, one above the other.

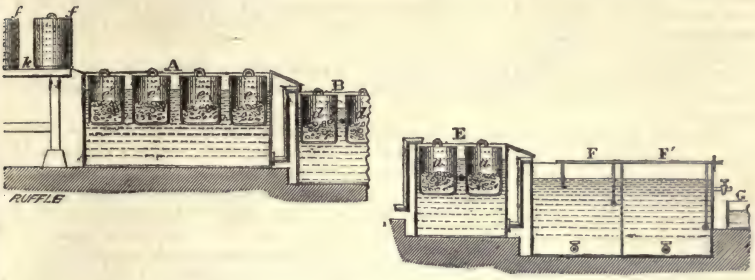


FIG. 157.

The uppermost tank is of cast iron, and twice as large as any of the others. It is connected with the next tank by a tube, the mouth of which terminates about 6 inches above its bottom, and each of the other tanks has a similar communication with its neighbour; so that a liquid, poured in at A, passes out eventually from E into F.

The outflow pipes may be replaced by the contrivance represented in section and plan by fig. 158; it consists of a channel, open above and below, and the upper end terminating above the level of the liquid, the lower end reaching to within 8 in. of the bottom of the tank. The liquid of the tank (A) passes into the channel at the lower end (A′), and flows out at the upper end (A″), into the second tank (B), whence it escapes through a similar channel (B′ B″) into the following tank, and so on to the last one.

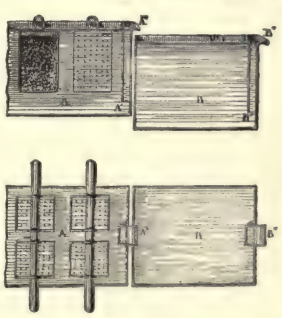


FIG. 158.

The lowest tank (E), fig. 157, communicates in like manner with six wide sheet-iron tanks (F F′), of which two only are shown in the drawing. These tanks are called the clearing or settling tanks. They are all at the same level, and they communicate with each other by means of a tube placed 4 inches below the upper rim. They are emptied by means of a siphon.

The lixiviating operation is conducted as follows:—Ball soda, broken into small pieces, is placed in perforated metallic boxes (*e e*, *d d*, etc.), and the vessels (A, B, C, D, E), having been previously filled with water, a couple of these perforated boxes are hung in the first lixiviating tank (E) by a bar thrust through their handles. After they have remained there for 25 or 30 minutes, they are taken out and placed in the tank (D), a couple of fresh boxes being at the same time suspended in E. This operation is continued at regular intervals; so that in the course of about 8 hours, when 14 lixiviating tanks are used, the first boxes (*e′ e′*, *e e*), containing the raw or ball soda, are suspended in the large tank (A), having by this time passed through all the other lixiviating tanks, while the boxes (*f f*) are taken out and placed upon an inclined board (K) to drain into the tank. After about half an hour the residue is removed from these latter boxes, and placed in trucks for removal from the works, while *e′ e′* take the place of *f f*, *e e* the place of *e′ e′*, etc., a couple of fresh boxes being then suspended in E. Each time this is done, a quantity of water, equal to double the volume of soda, is poured into the tank (A). The water displaces the heavy liquor at the bottom, and causes it to flow into the following tank (B), and displace the heavy liquor from it into the next tank (C), and so on until an almost saturated solution is found in the settling vessel (F F′). After the mechanical impurities are deposited in the settling tanks, the liquor is drawn off into the evaporating pans (G, H, I, J, fig. 159, page 265).

Supposing each couple of sieve boxes to hold a charge of 2 cwt. of crude soda, and

they are freshly charged every half-hour, a lixiviating apparatus of 15 tanks would be capable of lixivating $4\frac{3}{4}$ tons of raw soda in 24 hours.

Instead of this form of apparatus another is sometimes used, in which the lixiviating tanks are twice as long, and divided in the middle by a double partition into two equal parts, a couple of perforated boxes containing crude soda being placed in each division. The liquid flows out of the first division of the first tank through an aperture near the bottom of the first partition, rises in the space between it and the second partition, and flows through an opening in the upper part of the second partition into the second division of the tank, from whence it passes into a second tank of the same kind, etc. The liquor is heated by steam pipes passed between the double partition.

Another method consists in placing the crude soda upon a perforated shelf, about 8 inches from the bottom of the tanks, instead of putting it into perforated boxes or baskets.

Schank's lixiviating apparatus is especially suitable for lixiviation on a large scale, and consists of a row of 4, 6, or 8 sheet-iron tanks, each having a depth of $8\frac{1}{2}$ ft. and a height of $6\frac{1}{2}$ ft. Near the bottom of each tank is a perforated shelf. The first tank communicates with the second by means of a tube, bent at right angles, one end of which terminates near the bottom of the first tank, while its other extremity terminates in the upper part of the second tank. All the other tanks are connected together in like manner. A cock, placed above each tank, supplies water, while another cock, placed between the perforated shelf and the bottom of each tank, serves for drawing off the liquor. A system of four lixiviating tanks is generally so arranged that, when the fourth tank is charged with fresh crude soda, the third tank contains soda that has been once lixiviated, the second soda that has been twice lixiviated, and the first soda almost entirely lixiviated. Fresh water is run into the first tank, passing from it into the second tank, and so on to the last tank. After having been allowed to stand some hours, the liquor is drawn off from the last tank into the settling tanks, and during this operation the communication between the first and last tank is interrupted. So soon as the raw soda in the first tank is completely lixiviated, the tank is emptied and charged afresh with raw soda. Fresh water is then run into the second tank; from there into the fourth and last tanks; then into the first tank containing the fresh crude soda, and then the highly concentrated liquor is drawn off into the settling vessels, during which operation the communication between the first and second tanks is interrupted. This method of proceeding secures a methodical lixiviation of raw soda without it being necessary, as in the other forms of apparatus, that the soda should be moved, thus saving considerable manual labour. Besides this, the apparatus yields a clearer lye, and the cost of the apparatus, as well as the wear and tear, are less than in the forms of apparatus formerly used.

The liquor obtained has a specific gravity varying between 1·178 and 1·225, according as a hard or soft kind of raw soda has been lixiviated.

Concentration of the Liquor.—This operation is carried out in iron pans, heated either from beneath or by passing over them the hot air from a reverberatory furnace.

The liquor contains besides sodium carbonate varying amounts of common salt, sodium sulphate, caustic soda, etc. Upon evaporation tolerably pure sodium carbonate ($Na_2CO_3 + H_2O$) separates first, while that subsequently deposited is less pure. By removing the first deposit, and continuing the evaporation while adding fresh liquor, a deposit is obtained of nearly pure soda, containing 95 per cent. of sodium carbonate, until the operation has been continued so long that the foreign substances are concentrated in the mother liquor to such an extent that they are deposited together with the sodium carbonate. When this point has been reached, the mother liquor, containing only very small quantities of sodium carbonate, is removed, and the pans are charged again with fresh liquor.

An evaporating apparatus, in which the hot air from the furnace serves to heat and partly evaporate the liquor, is represented by figs. 159 and 160. The pans (G, H, I, J, K) are heated by the hot air escaping from the furnace (*i*). The soda liquor passes from the settling tanks first of all into the pan (G); from thence into (H, I, etc.), the temperature constantly increasing until concentrated liquor passes into the pan (K), heated directly by the fire (*i*), where crystals of sodium carbonate are at once deposited. The first portions of the deposited salt are somewhat impure, from containing the insoluble constituents held in suspension in the liquor. The following portions are pure, and are taken out from the pan as soon as deposited by means of perforated ladles, and laid to drain upon a wooden strainer lined with lead.

The forms of the pans used in evaporating the lyes vary considerably. Sometimes rectangular and oval pans with a flat bottom are employed, and sometimes oval pans with a round bottom. The pans are heated either by a special fire, or by the hot air escaping from the reverberatory soda furnaces. The liquor is passed directly from the

clearing vessels into the pans, heated as quickly as possible, and, as soon as deposition of soda begins, stirred to prevent the soda burning to a hard cake upon the bottom of the pan. When a sufficient quantity of deposit has been formed, it is removed by

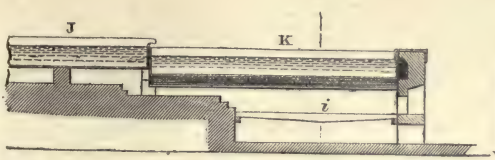


FIG. 159.

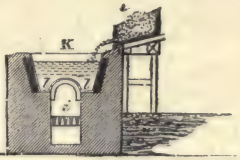


FIG. 160.

rakes, and either laid upon strainers or upon an inclined shelf, so that the mother liquor drains back into the evaporating pan. A more useful kind of pan is furnished with a groove round the side, where the temperature of the pan is not so great. The deposited soda is raked by the workman into this groove, and when it is full the salt is drawn out with a perforated ladle having a form corresponding to the shape of the groove, the deposit being, as before, laid on strainers to drain.

In proportion as the level of the liquor in the pan sinks, owing to the removal of the salt, fresh liquor is run into the pan.

A very important method of evaporation is that in which the hot air from the black ash or balling furnaces is made to pass over the surface of the liquor in the evaporating pans (*vide* p. 264). This method of evaporation admits of being adapted to every soda furnace. The method adopted in the case of the ordinary furnace has been described on p. 260; that adopted in the case of the cylindrical furnace on p. 260, fig. 154, in which G is the pan space through which the hot air from the cylinder is made to pass over the surface of the pan. This method of evaporating the liquor has many advantages over those above described; for without taking into account the fact that fuel is spared, it is clear that the work and attention required are less, inasmuch as, by heating from above, no danger is incurred of the soda burning to the bottom of the pan, and consequently no stirring is required. Besides this, it is not necessary to remove the deposited soda so often as is required in the case of pans heated from beneath.

Direct heating of the Lye to dryness.—This method of treating mother liquor yields a product containing all the constituents of the black ash. The operation is carried out in a reverberatory furnace (fig. 161), the hearth (S) of which is made of fire bricks,

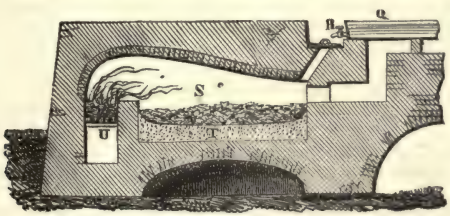


FIG. 161.

over which a thick coating of sodium carbonate (T) is well rammed, so as to prevent the liquor from coming into contact with the bricks. The fuel burnt in the furnace (U) is coke; as soon as the furnace has become thoroughly red hot, the liquor is run out of the pan (Q) through the cock (R) by a cast-iron tube passing through the arch of the furnace, on to the hearth (S). Upon the liquor coming in contact with the hot layer of soda upon the hearth, a lively ebullition takes place, the mass froths up and soon dries. Constant stirring is requisite, partly in order to accelerate the drying, and partly to render the soda pulverulent. So soon as a large quantity of dry salt has been produced, the flow of liquor is interrupted by closing the cock (R), the salt is removed from the furnace, and the operation recommenced.

The composition of soda ash thus evaporated to dryness varies considerably; the following table gives the result of two analyses of such soda by J. Brown.

	I.	II.
Sodium carbonate	68·907	65·513
Hydrate of soda (caustic soda)	14·433	16·072
Sodium sulphate	7·018	7·812
„ sulphite	2·231	2·134
„ thiosulphate	traces	traces
„ sulphide	1·314	1·542
„ chloride	3·972	3·862
„ aluminate	1·016	1·232
„ silicate	1·030	0·800
Insoluble matter	0·814	0·974
	100·735	99·941

The salt is next calcined in order to convert sodium sulphide into sulphate, and a part of the caustic soda into sodium carbonate, as well as to secure the destruction of organic matter, and to render the salt anhydrous. For this purpose it is heated in a reverberatory furnace fed with coal, care being taken to stir the mass constantly, so as to renew the surface exposed to the hot air. The mass is heated until it begins to cohere, but not until it melts, in which case it would attack the hearth of the furnace, and be rendered impure by the formation of sodium silicate and aluminate. The following table gives the results of two analyses of calcined soda ash by J. Brown.

	I.	II.
Sodium carbonate	71·614	70·461
Caustic soda	11·231	13·132
Sodium sulphate	10·202	9·149
„ sulphite	1·117	1·136
„ chloride	3·051	4·279
„ aluminate	0·923	0·734
„ silicate	1·042	0·986
Insoluble matter	0·316	0·464
	99·496	100·341

In order to convert the caustic soda into sodium carbonate, the soda ash is mixed before calcination with finely pulverised charcoal or with sawdust, and the carbonic acid yielded by these substances during the calcination combines with the caustic soda to form sodium carbonate; for this reason the operation is termed carbonating.

To obtain soda crystals, pure black ash is first of all prepared, as little charcoal powder as possible being added in the balling operation, to secure as complete conversion as possible of the caustic soda into sodium carbonate. The addition of rather more chalk than usual is also advantageous for the more complete conversion of sodium sulphate into carbonate. The ball soda obtained is lixiviated in the usual way, and the black ash liquor, concentrated to sp. gr. 1·267, is then run into crystallising vessels, which are from three to six feet long, one and a half wide, and ten to thirteen inches deep.

When the liquor has thoroughly cooled crystallisation commences, and it goes on more rapidly the cooler the surrounding atmosphere. On this account the preparation of soda crystals is very conveniently performed in winter time.

When the crystallisation is complete, the mother liquor is run off by drawing out a plug fixed in the bottom of the crystallising vessel, and having a handle extending above the level of the liquid. The crystals are then detached from the sides of the crystallising vessels with the aid of a chisel, and are placed upon strainers to drain. They are usually somewhat impure and discoloured, but answer for many purposes. When pure soda crystals are required, the salt is again dissolved in hot water, mixed with $\frac{1}{1000}$th part of its weight of lime, which forms calcium carbonate, and carries down with it the mechanical impurities contained in the solution. After the liquor thus obtained has become quite clear, it is run into crystallising vessels, placed in a cool position, and as soon as the crystallisation is complete the crystals are taken out, drained in perforated troughs lined with lead, and, after having been left for a short time to dry in the air, they are packed. If left too long exposed to the air, they effloresce or become dull on the surface, owing to loss of water of crystallisation.

Soda crystals are often prepared from soda ash that has been mixed with a small quantity of finely pulverised charcoal and calcined for the purpose of converting the caustic soda into sodium carbonate. The calcined mass is dissolved in boiling water in large iron pans heated by passing steam into the liquid until a solution is obtained having a specific gravity of 1·216; this is run into settling vessels, and when clear evaporated to a specific gravity of 1·256 to 1·267, and then run into the crystallising vessels, either cast-iron boxes or pans, preference being now generally given to the pans.

In order to remove organic substance the liquor is treated with bleaching powder, before allowing it to crystallise, and during this operation it must not be allowed to cool below 33°, otherwise some sodium carbonate would be precipitated.

The troublesome work of detaching with a chisel the soda crystals lining vessels may be avoided by placing the boxes from which the mother liquor has been run off in a vessel that can be filled with boiling water, so that the crystals adhering to the surfaces of the boxes are melted and thus detached.

Soda that is to be used in the manufacture of white glass is again calcined. The following table gives the results of analyses by Brown of soda ash before and after calcination:

	Crystallised Soda		Cyrstallised Soda after calcination	
	I.	II.	I.	II.
Sodium carbonate	36·476	36·931	98·120	07·984
„ sulphate	0·943	0·542	1·076	1·124
„ chloride	0·424	0·314	0·742	0·563
Water	62·157	62·213	—	—
	100·000	100·000	99·938	99·671

Soda crystals, being tolerably pure, may be conveniently used for preparing chemically pure sodium carbonate, for which purpose it is only necessary to dissolve the crystals in hot water and allow the solution to crystallise in a cool place. The operation is repeated until the crystals produced, when dissolved in water made slightly acid with nitric acid, cease to give a reaction with silver nitrate (chlorine) or with barium nitrate (sulphuric acid).

Kopp's method of preparing sodium carbonate from sodium sulphate, and at the same time recovering the sulphate, consists in heating the sulphate to redness in a reverberatory furnace together with ferric oxide and carbon, allowing the product thus obtained to disintegrate in a moist atmosphere, rich in carbonic acid, lixiviating with water, and reconverting the undissolved residue of ferrous sulphide into ferric oxide by roasting it, the sulphurous acid thus produced being used for preparing sulphuric acid. Kopp assumes the following chemical changes to take place:—

α. Sodium sulphate, ferric oxide, and carbon yield when heated to redness a double sulphide of sodium and iron, as well as carbonic oxide and carbonic acid:

$$3Na_2SO_4 + 2Fe_2O_3 + 16C = Fe_4Na_6S_3 + 14CO + 2CO_2.$$

β. The double sulphide of sodium and iron is converted by the action of oxygen. water, and carbonic acid into sodium carbonate, and another double sulphide of iron and sodium containing less sodium:

$$Fe_4Na_6S_3 + 2O + 2CO_2 = Fe_4Na_2S_3 + 2Na_2CO_3.$$

γ. The compound $Fe_4Na_2S_3$ yields upon roasting ferric oxide, sodium sulphate, and sulphurous acid:

$$Fe_4Na_2S_3 + 14O = 2Fe_2O_3 + Na_2SO_4 + 2SO_2.$$

According to Kopp, 125 parts of sodium sulphate are mixed with 80 parts of ferric oxide and 55 parts of charcoal powder, the mixture being heated in an ordinary balling furnace until it has assumed the consistency of a thin dough. It is then taken out and allowed to cool in well-closed iron boxes. The blocks when cold are placed on a grating in a chamber furnished with draught holes, into which chamber moist carbonic acid gas is passed from beneath the bars of the grating. The carbonic acid is prepared by burning coke, and before the gas reaches the bars of the grating supporting the blocks it is moistened by being passed through tubes wetted internally and cooled from outside. The effect of the moistened carbonic acid upon the blocks is to cause them to crumble and fall down between the bars of the grating, where they are acted upon by further portions of carbonic acid. The crumbling of the blocks and the

consequent separation of the disintegrated portions from the solid blocks is of great importance, inasmuch as an ignition of the entire mass would otherwise be apt to occur. The disintegrated mass is separated with sieves from the siliceous fragments from the furnace, and lixiviated in the usual way. This process when properly conducted yields, upon evaporation of the crude soda liquor, soda ash containing as much as 95 per cent. of sodium carbonate.

The residue from the lixiviation consists chiefly of ferrous sulphide. It is either dried and further operated upon in this state, or made into bricks by the aid of pressure. In either case it is eventually roasted, and the sulphurous acid evolved conducted into leaden chambers for making sulphuric acid, which is used for converting fresh quantities of common salt into sodium sulphate. The residual ferric oxide from the incineration of the ferrous sulphide is again used for converting sodium sulphate into carbonate. Since the ferric oxide thus obtained is always contaminated with the sulphates of sodium, calcium, and magnesium, it is best to wash it with water before using it again for the conversion of sodium sulphate into carbonate, in order to extract the sodium sulphate, and then with dilute hydrochloric acid, which removes the sulphates of calcium and magnesium. Thus treated, the ferric oxide is available for use for a very considerable length of time.

Pelletan's process consists in converting sodium sulphide dissolved in water into carbonate by passing carbonic acid into the solution:

$$Na_2S + CO_2 + H_2O = Na_2CO_3 + H_2S.$$

For this purpose sodium sulphate is reduced to sulphide by heating it with charcoal, the product is lixiviated, and carbonic acid passed through the liquor obtained. The sulphuretted hydrogen given off admits of being again treated for sulphuric acid by passing it through ferric oxide. Ferrous sulphide is thus formed, which is then roasted, and the sulphurous acid is conducted into lead chambers for conversion into sulphuric acid. Klemm and Böhringer bring the sulphuretted hydrogen into contact with sulphurous acid, by which means sulphur is deposited in the free state:

$$SO_2 + 2H_2S = 3S + 2H_2O.$$

This method has this disadvantage, that in consequence of the formation of polysulphides, which are difficultly decomposed by carbonic acid, the soda obtained is contaminated with sulphur.

Wilson decomposes sodium sulphide liquor by boiling it with double sodium carbonate; Bower by digesting it with ammonium carbonate, in which process bicarbonate of sodium is obtained and ammonium sulphate as by-product.

Sodium sulphide may also be decomposed by boiling it with hydrate of alumina, which is obtained as a by-product in the preparation of soda from cryolite. Sodium aluminate is thus formed, and sulphuretted hydrogen, which is absorbed by ferric oxide and used for preparing sulphuric acid. The sodium of the sodium aluminate is then converted into carbonate by treating the liquor with carbonic acid.

Prückner decomposes sodium sulphide solution with cupric oxide, by which means a precipitate is formed consisting of cupric sulphide, the residual liquor consisting of a solution of caustic soda. The cupric sulphide is roasted to obtain sulphurous acid and sulphuric acid, while the caustic soda is mixed with sawdust and the mixture calcined, so as to convert the caustic soda into sodium carbonate. The cupric sulphate is again treated for cupric oxide.

A method proposed for converting sodium sulphate into carbonate by acting upon it with barium carbonate failed on account of the difficulty experienced in effecting the decomposition either in the moist or dry way. Another method proposed by Wagner consisted in using barium bicarbonate, or a mixture of it and the simple carbonate, obtained by passing carbonic acid into water containing barium carbonate in suspension. This also has proved unsuccessful.

Caustic baryta is at present too dear for the purpose of converting sodium sulphate into carbonate, although the decomposition is very complete.

Ungerer describes a method of preparing soda in which caustic strontia is employed for converting sodium sulphate into carbonate. This method is worth notice on account of the fact that both the sulphuric acid of the Glauber's salt, as well as the caustic strontia employed for the decomposition, admit of being again used. A saturated solution of ammonium sulphate is mixed with its equivalent of common salt and the mixture boiled for a short time. The hot solution deposits sodium sulphate, which is removed, and the residual liquor when sufficiently cooled deposits sal ammoniac, which is likewise removed. The mother liquor is then boiled down and yields a second crop of sodium sulphate. The sodium sulphate is dissolved in water and treated with caustic strontia; strontium sulphate is thus precipitated, while caustic soda remains in solution, and is treated with carbonic acid to form sodium carbonate. Ammonium chloride,

obtained by decomposing ammonium sulphate with common salt, is then heated to redness with calcium carbonate, and thus converted into ammonium carbonate, with which the strontium sulphate suspended in water is heated for some time. By this means strontium carbonate is formed and ammonium sulphate, which is again used for converting sodium chloride into sulphate. The strontium carbonate is mixed with carbon and heated to redness in a reverberatory furnace, while at the same time steam is passed through the mixture, and by this means it is again converted into caustic strontia, which is used for decomposing sodium sulphate.

A method suggested by Weldon consists in preparing sodium sulphate by treating common salt with magnesium sulphate, converting the sodium sulphate into sodium fluoride and acid sodium sulphate by treating it with hydrofluoric acid. The two salts are then separated by crystallisation, and the sodium fluoride converted into caustic soda by acting upon it with caustic lime. The caustic lime may be replaced by the magnesia, obtained, together with Glauber's salt and hydrochloric acid, as a by-product in treating sodium chloride with magnesium sulphate.

Jean melts together sodium sulphate, fluorspar, calcium carbonate, and carbon, so as to produce sodium fluoride, calcium sulphate, carbonic oxide, and caustic lime. The sodium fluoride is dissolved out by water and treated with caustic lime.

Baader converts sodium sulphate into carbonate by melting it with silica (sand) and carbon; the sodium silicate formed is dissolved out with water, and decomposed by carbonic acid.

Puissant's method of preparing soda together with lead carbonate consists in passing carbonic acid through a boiling solution of sodium sulphate, containing barium carbonate in suspension. In this way barium sulphate and sodium carbonate are formed. The sodium carbonate solution is decanted from the barium sulphate, treated with lead sulphate, heated to the boiling point, and again treated with carbonic acid, when lead carbonate and sodium sulphate are formed, the latter being again used for preparing sodium carbonate, etc.

Preparation directly from Sodium Chloride.—The oldest method of preparing soda artificially consisted in the direct conversion of common salt into caustic soda by filtering it through litharge. The caustic soda was then converted into sodium carbonate, by exposing it for some time to the air. This method, originated by Scheele, has been often patented, but has not met with much success.

Blanc and Bazille's method consists in decomposing common salt by heating it to redness with sand in a current of steam. A mixture of 280 parts common salt and 200 parts sand is heated to redness in a cast-iron retort, into which steam is passed by means of a pipe with small holes. By this means the sodium chloride is decomposed according to the equation:

$$2NaCl + SiO_2 + H_2O = Na_2SiO_3 + 2HCl.$$

The hydrochloric acid, escaping with the steam and a small quantity of sodium chloride, passes through a stoneware tube into a chamber where the sodium chloride is condensed, and the hydrochloric acid is either condensed in ordinary condensing bottles or in a stoneware trough, the bottom of which is covered with water. The solid product left in the retort is so difficultly soluble in water that it requires to be melted with $\frac{3}{5}$ of its weight of soda; a readily soluble basic sodium silicate is thus obtained, and when dissolved in water, is converted into sodium carbonate by passing carbonic acid through the solution.

Gossage's method consists in passing the hot air from a coal fire through a flue where it is mixed with steam, and then over a surface of common salt into the upper part of a shaft furnace contracted towards its lower extremity, and filled with pieces of quartz. The sodium chloride volatilised with the hot air and steam, on coming into contact with the red-hot quartz, is converted into sodium silicate and hydrochloric acid.

Tilghman's method consists in passing superheated steam through melted sodium chloride, which causes volatilisation of the salt, together with the steam. This mixture of steam and salt vapour is then passed into an iron cylinder filled with pieces of red-hot alumina. Sodium aluminate is thus formed, which is treated for soda with carbonic acid.

Dyer, Grey, and Harrison's method consists in treating a saturated solution of common salt with finely powdered ammonium sesquicarbonate, or, still better, with the bicarbonate. In this way acid sodium carbonate is formed, which separates owing to its sparing solubility in water, together with a small quantity of ammonium carbonate, and ammonium chloride remains dissolved. The precipitate, deprived of adhering mother liquor as much as possible by filtering and pressing, is then dried and heated to redness, so as to volatilise the adherent ammonium carbonate, and convert the double sodium carbonate into simple carbonate. The mother liquor, contain-

ing ammonium chloride, is evaporated to dryness; and the residue heated to redness with calcium carbonate to convert it into ammonium carbonate.

An excellent modification of the above method consists in using caustic ammonia in the place of ammonium sesquicarbonate or bicarbonate. Caustic ammonia is mixed with the solution of common salt, and carbonic acid forced into the mixture under pressure. A precipitate of acid sodium carbonate is thus formed, and is separated from the mother liquor by a centrifugal machine, purified by washing, and dried. The mother liquor is mixed with slaked lime, and boiled as long as ammonia is evolved. The ammonia is in its turn passed into a solution of common salt for the decomposition of the latter, in the way already stated.

A number of other methods have been suggested for the direct conversion of common salt into sodium carbonate, but none of them have as yet met with industrial success. Among such methods may be mentioned Samuel's, which consists in precipitating acid sodium oxalate from a solution of common salt, by the addition of oxalic acid. The precipitate is then boiled with slaked lime, by which calcium oxalate and caustic soda are formed. Spilsbury and Maugham precipitate the sodium contained in common salt as silico-fluoride, by treating a solution of common salt with fluosilicic acid. The sodium silico-fluoride is then decomposed by the aid of heat into sodium fluoride and silicon fluoride; the former, boiled with slaked lime, forms calcium fluoride and caustic soda. The fluosilicic acid is obtained either by heating to redness a mixture of sand, clay, and fluorspar, or as a by-product when silicon fluoride is passed into water. The calcium fluoride obtained by the decomposition of the sodium fluoride with lime is also treated for fluosilicic acid. Kessler patented a method for the conversion of common salt into sodium carbonate, which consisted in first of all forming sodium chromate by heating common salt to redness with chromium oxide, and passing steam over the mixture. The sodium chromate was then mixed with carbon, and the mixture heated to redness, so as to form chromium oxide and sodium carbonate. The product only required lixiviating to separate the soluble sodium carbonate from the insoluble chromium oxide, which was then ready for decomposing a fresh quantity of sodium chloride.

Preparation from Cryolite.—The composition of cryolite is represented by the formula AlF_3, 3NaF. It occurs in large deposits in Greenland, whence it is chiefly exported to Germany and Denmark.

Thomsen decomposes cryolite into sodium aluminate, calcium fluoride, and carbonic acid by heating it with calcium carbonate:

$$AlF_3 + 3NaF + 3CaCO_3 = AlNa_3O_3 + 3CaF_2 + 3CO_2.$$

The sodium aluminate is dissolved out with water and decomposed with carbonic acid, hydrate of alumina being separated:

$$2AlNa_3O_3 + 3CO_2 + 3H_2O = 3Na_2CO_3 + 2AlH_3O_3.$$

The aluminum hydrate thus obtained is treated with sulphuric acid to form aluminum sulphate (see page 308).

For this purpose 100 parts of cryolite reduced to a very fine powder, are mixed with 127 parts of equally finely powdered calcium carbonate. The mixture is heated on the hearth of a reverberatory furnace, fired with coke, and continually stirred until the mass begins to cake together. It is then removed from the furnace, reduced to powder, and lixiviated with hot water. The liquor, while still hot, is run into closed cylinders, placed in a horizontal position and furnished with a condensing arrangement, where it is treated with carbonic acid obtained from the hot air escaping from the reverberatory furnace. The contents of the absorption cylinders are emptied into clearing vessels where the aluminum hydrate is deposited. The clear liquor is then drawn off and treated either for crystallised or calcined sodium carbonate. The deposit of aluminum hydrate is washed several times with fresh water, and then placed in a wooden vat lined with lead, where it is saturated with warm sulphuric acid (80°–90°), specific gravity 1·490. The clear solution is decanted off and evaporated in copper pans until a product is obtained having a composition represented by the formula:

$$Al_2S_3O_6 + 18H_2O.$$

It is not possible by washing to remove the last traces of soda from the aluminum hydrate, and consequently the aluminum sulphate thus obtained invariably contains some sodium sulphate. It is however entirely free from iron.

Sauerwein boils finely powdered cryolite with milk of lime so as to form sodium aluminate and calcium fluoride:

$$(AlF_3 + 3NaF) + 3CaO = AlNa_3O_3 + 3CaF_2.$$

The clear liquor thus obtained is deprived of alumina by treating it with an excess

of finely powdered cryolite and continually stirring; by this means aluminum hydrate and sodium fluoride are formed:

$$AlNa_3O_3 + (AlF_3 + 3NaF) + 3H_2O = 2AlH_3O_3 + 6NaF.$$

The aluminum hydrate is heated as above described with sulphuric acid for aluminum sulphate, and the sodium fluoride is treated with caustic lime for caustic soda.

Weber's method consists in treating cryolite with sulphuric acid, by which means aluminum sulphate and sodium sulphate are formed according to the equation:

$$2(AlF_3 + 3NaF) + 6H_2SO_4 = Al_2SO_4 + 3Na_2SO_4 + 12HF.$$

The evaporation of the liquor yields in the first instance crystals of sodium sulphate, and the mother liquor is then treated for aluminum sulphate.

The mineral called bauxite, consisting of from 60 to 75 per cent. of alumina and 12 to 25 per cent. of ferric oxide, together with some silica and water, is also used in the manufacture of soda, although it yields neither soda nor carbonic acid. Balard heats bauxite to redness with sodium sulphate, so as to form sodium aluminate and aluminum hydrate. Another method consists in passing superheated steam over a mixture of bauxite and common salt, by which means sodium aluminate and hydrochloric acid are produced.

Sodium nitrate, or Chili saltpetre, commonly used in the preparation of nitric acid, furnishes sodium sulphate, which admits of direct conversion into carbonate by Leblanc's method.

A number of attempts have also been made to obtain sodium carbonate from sodium nitrate in a more direct and simple manner. 1. By means of potassium carbonate, so as to obtain potassium nitrate and sodium carbonate. 2. Walz suggests heating a mixture of sodium nitrate and calcium carbonate to redness in a current of steam. Nitric acid escapes with the steam, and is condensed in suitable vessels; while the residue in the retorts consists of a mixture of sodium and calcium carbonates. This residue is lixiviated, yielding soda liquor. 3. Sodium nitrate may also be decomposed by caustic potash, yielding caustic soda and potassium nitrate; and (4) by igniting sodium nitrate with carbonaceous materials.

Uses.—Soda, or sodium carbonate, is an article of very extensive consumption. Amongst the uses to which soda is put may be mentioned the manufacture of glass, the washing of wool and silk, the preparation of aerated water, soap-making, etc. Further, it is used in the preparation of sodium bicarbonate, and of a number of sodium salts, as well as various carbonates, as an agent in the chemical laboratory for various purposes, and as a medicine.

Utilisation of Soda Waste.—The residue from the lixiviation of ball soda, known as soda waste, varies considerably in composition, as shown by the following table, giving the results of analyses by Brown and Richter.

	Brown's Analysis	Richter's Analyses (from the Chemical Works at Sarau, in Silesia)		
		I.	II.	III.
Calcium carbonate	24·220	23·18	22·24	24·02
„ sulphide	8·527	37·62	38·04	39·10
„ oxysulphide	20·363	—	—	—
„ sulphate	4·281	1·68	1·01	1·38
„ hyposulphite	traces	2·69	3·02	2·35
„ sulphite	—	0·74	0·31	0·63
„ disulphide	3·583	—	—	—
„ oxyhydrate	3·583	—	—	—
Sodium carbonate	1·309	—	—	—
Soda	—	2·52	2·10	1·86
Lime	—	6·49	7·00	7·25
Magnesium carbonate	5·987	—	—	—
Magnesia	—	0·64	0·51	0·70
Alumina	—	2·11	2·02	2·00
Ferric oxide	5·716	—	—	—
Ferrous sulphide	—	1·88	1·75	2·01
Carbon	12·709	5·41	6·00	6·39
Sand	5·746	7·74	6·82	7·21
Silica (in combination)	—	4·24	4·03	4·62
Water	2·100	2·32	3·29	1·51

When soda waste is allowed to lie exposed to the air, a portion of its calcium sulphide is converted into calcium carbonate and disulphide, which yield by further oxidation calcium thiosulphate, and this decomposes rapidly into calcium sulphite and free sulphur. Upon continuing the oxidation the calcium sulphite is converted into sulphate. The sulphur liberated from calcium thiosulphate is either oxidised by contact with atmospheric air, forming sulphurous acid, or else it combines with calcium sulphide to form bisulphide, which yields a further quantity of calcium thiosulphate. The exposure of soda waste to the atmosphere also gives rise to the formation of sodium thiosulphate, partly by the oxidation of sodium sulphide, and partly by the mutual decomposition of calcium thiosulphate and sodium carbonate to sodium thiosulphate and calcium carbonate. The higher polysulphides of calcium and sodium may also be produced by the action of free sulphur, liberated from calcium thiosulphate, upon the monosulphides of calcium and sodium. The heat produced by the oxidation of soda waste in the atmosphere is frequently sufficient to cause an ignition of the entire mass.

Soda waste is chiefly used for the recovery of the sulphur contained in it. The most important methods by which this is done are those of Hofmann, Buquet, Schaffner, and Mond.

Schaffner's method involves the following operations :—

1. *Preparation of the liquor containing Sulphur.*—For this purpose soda waste is exposed in lumps for several weeks to the action of the air, care being taken that the oxidation does not go too far. It must be just sufficient to cause the conversion of sulphides into polysulphides and thiosulphates without formation of calcium sulphate, for any sulphur converted into that compound would be entirely lost. The requisite degree of oxidation is recognised by the dark grey colour of the mass, which is then lixiviated with water, and the residue again exposed to oxidation in the lixiviating tubs by passing through it a stream of warm air. The lixiviation is repeated after each oxidation. The salts dissolved out consist chiefly of polysulphides, and thiosulphates of sodium and calcium, and it is easy to regulate the oxidation in such a way that sulphides and thiosulphates are produced in equal proportion.

2. *Separation of the Sulphur.*—This operation depends upon the facts that thiosulphates treated with hydrochloric acid are decomposed into free sulphur and sulphurous oxide :

$$CaS_2O_3 + 2HCl = CaCl_2 + H_2O + S + SO_2.$$

The sulphurous oxide reacts upon the polysulphides, liberating another portion of sulphur, while at the same time fresh quantities of thiosulphates are formed ; thus :

$$2CaS_3 + 3SO_2 = 2CaS_2O_3 + 5S.$$

The decomposition of the liquor by means of hydrochloric acid is carried on in one of two close cylinders of cast iron or stone, the gaseous products of decomposition being passed alternately into one or other of the two vessels. Each vessel has four openings above, one of which serves for the admission of hydrochloric acid, another for the escape of gaseous products, while the other two effect the alternate transmission of the gaseous products from one cylinder into the other. A continual exchange of sulphurous acid from one cylinder into the other is thus kept up, and thus the entire quantity of sulphur contained in the liquor is deposited. The deposited sulphur has a fine granular structure and admits of easy filtration.

3. *Purification of the Sulphur.*—The precipitate thus obtained contains adherent calcium chloride and gypsum, and to remove these impurities it is mixed with water in an iron cylinder, closed at both ends and slightly inclined, so that one end is lower than the other. Steam at a pressure of $1\frac{3}{4}$ atmospheres is then admitted into the cylinder to melt the sulphur, the heat required being about 110°—115°. In order to saturate any free acid or to cause the solution of any arsenic that might be present, some milk of lime is added. The molten sulphur collects in the bottom of the cylinder, flowing towards the deepest part of the inclined cylinder, where it is tapped off into moulds.

In places where hydrochloric acid is dear, the residue from the preparation of chlorine is used instead of acid in the treatment of the liquor from soda waste. But since this residue contains ferric chloride, which from its action upon sulphurous acid would cause a loss of sulphur, the ferric chloride must first be got rid of by mixing the chlorine residue with soda waste until all the ferric chloride has been converted into ferrous chloride by the sulphuretted hydrogen of the waste. The liquor thus prepared is then used for the decomposition of the soda waste liquor.

At the Aussig soda works, Schaffner recovers in this way as much as 60–65 per cent. of the sulphur contained in soda waste. The sulphur thus recovered is used in the preparation of sulphuric acid, which is used to make sodium sulphate, etc.

Mond's method is very similar, and is extensively carried out in this country. The oxidation of the soda waste is accelerated by forcing air through the mass by means of a fan. The decomposition by hydrochloric acid is effected by mixing a definite quantity of hydrochloric acid with an excess of the liquor containing sulphur, and then adding hydrochloric acid sufficient for complete decomposition. More liquor is then poured in, hydrochloric acid added, and so on until the vessel is filled. Hoffman accelerates the oxidation of the soda waste by sprinkling the heaps with manganese chloride; the sulphur is then separated by the method already described.

In places where the recovery of sulphur from soda waste has not been introduced, the soda waste is used for other purposes. It is employed, for instance, in some cases as manure, for which purpose complete oxidation of the sulphides of calcium to sulphates is necessary, and consequently the soda waste requires longer exposure to the atmosphere. Further uses made of soda waste consist in the preparation of hyposulphites of calcium and sodium; it is also employed in the making of roads, walls, bricks, a kind of Portland cement, etc.

ACID SODIUM CARBONATE (BICARBONATE).

Formula $NaHCO_3$. Molecular Weight 84.

Characters.—Sodium bicarbonate is a white crystalline powder possessing an alkaline taste and turning red litmus paper blue. When exposed to a moist atmosphere, it gradually gives up parts of its carbonic acid; by heating the salt loses half of its carbonic acid together with water and is converted into sodium monocarbonate. Sodium bicarbonate is sparingly soluble in water, 100 parts of water at 10° dissolving about 10 parts of the salt; at 40°, 13·35 parts; and at 70°, 16·69 parts. Upon heating an aqueous solution of sodium bicarbonate a little above 70°, part of the carbonic acid of the salt escapes, sodium sesquicarbonate remaining in solution, and for this reason an aqueous solution of sodium bicarbonate must not be boiled.

Sodium bicarbonate is an essential constituent of many kinds of mineral water.

Preparation.—Sodium bicarbonate is prepared by acting upon sodium monocarbonate with carbonic acid, the carbonic acid required for this purpose being either obtained from natural acidulous springs, or by acting upon chalk or marble with a dilute mineral acid. In some cases it is found convenient to make use of the carbonic acid escaping from lime kilns or produced in fermentation.

An apparatus for preparing sodium bicarbonate with the carbonic acid of acidulous springs is shown in fig. 162. The escaping carbonic acid is caught in a kind of bell jar (B), the water escaping through an outlet at the side. The carbonic acid passes through the tube (*d*) into the gasometer (C), and is then conducted by means of the

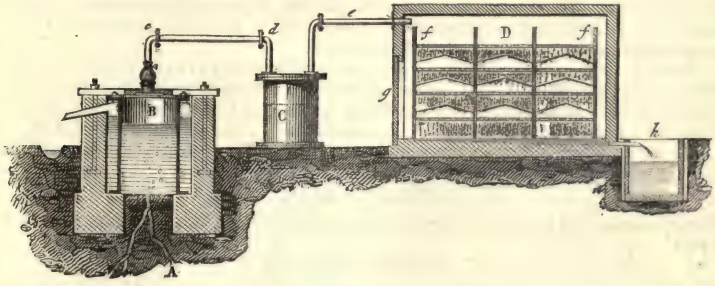


Fig. 162.

tube (*e*) into the absorption chamber (D), which is built of brick and fitted internally with a wooden rack supporting a number of frames over which pieces of woven fabric are stretched. Sodium monocarbonate is spread out upon these frames in a layer about 2½ or 3 inches thick, which thus exposes a considerable surface to the action of the carbonic acid. In cases where crystallised sodium monocarbonate is employed, nine equivalents of water are liberated during the formation of bicarbonate. On this account each frame is covered with a sloping roof, so that the water which trickles down from the frames and contains considerable quantities of sodium carbonate in solution, is carried off by passing over the sides of the roofs, and is conducted eventually along the bottom of the chamber into a tub (*h*) lined with lead. A number of chambers of

this kind are placed together, so that the unabsorbed carbonic acid escaping from the first chamber is conducted into the second and third, etc., for complete absorption. The charging and emptying of the chambers are effected through a lateral opening, which is closed during the operation by a plate (*g*).

The salt is dried either by passing through the chambers a stream of carbonic acid gas heated to 40°, or by burning charcoal on braziers placed in the chambers.

The carbonic acid used for preparing sodium bicarbonate is more frequently obtained by treating a carbonate with a mineral acid.

An apparatus for preparing sodium bicarbonate in this manner is represented by fig. 163. It consists of an iron generator (A) lined with lead, a wash vessel (G), and the wooden absorption vessels (J and L). The raw material from which carbonic acid is to be generated is placed in the generator (A) and mixed with water, the mixture kept

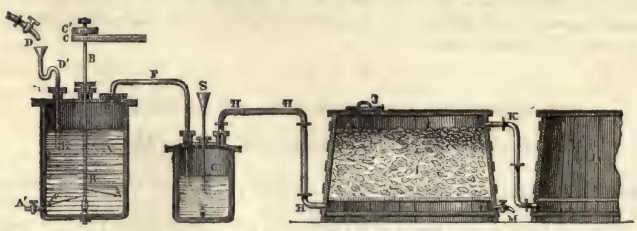


FIG. 163.

constantly stirred by the agitator (B B), driven by a strap on the fast and loose pulleys (C C′). By opening the tap (D) sulphuric acid of specific gravity 1·495 to 1·551 is run into the generator through the funnel (D′), and causes evolution of carbonic acid. The gas passes through the tube (F) into a wash vessel (G) filled to about one half with water, and from thence through the tube (H H H), entering the absorption vessel (J) through the perforated bottom, upon which the sodium carbonate is placed. As in the apparatus previously mentioned, a number of chambers of this kind are connected together so as to secure as complete an absorption of the carbonic acid as possible. The wooden vats are charged and emptied at (J). The water liberated when crystallised carbonate is employed collects below and is drawn off by a cock (M).

The carbonate most commonly employed for generating carbonic acid is calcium carbonate, in the form of chalk, marble, dolomite, etc., and it is decomposed either by sulphuric or hydrochloric acid. The use of magnesite, which was formerly the chief material employed for generating carbonic acid, has considerably decreased of late, owing to the fact that the kieserite mud of the Stassfurt potash works is such an excellent and cheap material for the preparation of magnesium sulphate (Epsom salts). Another material sometimes used for generating carbonic acid is witherite (barium carbonate), barium salts being then obtained as by-products.

Another acid sodium carbonate, commonly called sesquicarbonate, is formed under certain conditions, and it occurs naturally as a deposit from the water of lakes containing sodium carbonate, the materials known as trona and urao consisting chiefly of this salt. Its composition is represented by the formula $Na_4H_2(CO_3)_3$, and it may be regarded either as a compound of two molecules of neutral sodium carbonate with one molecule of carbonic acid

$$2Na_2CO_3 + H_2CO_3,$$

or as a compound of one molecule of neutral carbonate with two molecules of acid carbonate

$$Na_2CO_3 + 2NaHCO_3.$$

This salt crystallises in rhombic prisms which contain two molecules of water; it is less soluble than the neutral carbonate and more soluble than the acid carbonate.

TESTS FOR SODIUM BICARBONATE. *Qualitative Tests.*—The presence of sodium monocarbonate in sodium bicarbonate is ascertained by treating a small portion of a solution of the latter with a few drops of a solution of magnesium sulphate. A cloudiness or precipitate indicates the presence of sodium monocarbonate. The presence of chlorine is ascertained by adding a few drops of a solution of silver nitrate, together with a drop of nitric acid, to a solution of sodium bicarbonate. A white precipitate or cloudiness indicates the presence of chlorine. Sodium sulphate is found by testing a solution of sodium bicarbonate, previously acidulated with hydrochloric acid, with barium chloride, which, if sulphate is present, causes a white precipitate of barium sulphate.

Quantitative Tests.—In order to determine the precise amount of pure sodium bicarbonate in a sample of the latter, the salt is heated to expel as much as possible of the carbonic acid, and the volume of the carbonic acid carefully measured. Fig. 164 shows an apparatus for a determination of the above kind. A is a glass tube sealed at one end, into which is brought five grams of the salt to be operated upon. To the other end of the tube is attached a glass tube (CCC), fitted accurately into the mouth of the tube A by means of a good cock, the tube (CCC) being bent in the manner shown in the drawing and opening beneath the mouth of the graduated glass cylinder (D) of 1 litre capacity, the latter being filled with water and inserted in a vessel (B) likewise filled with water. A small quantity of oil is inserted into the graduated cylinder to prevent absorption of carbonic acid by the water. The sodium bicarbonate in A is now heated by the aid of a spirit or gas lamp, which causes an expulsion of carbonic acid, the latter passing through CCC into the graduated cylinder (D). The application of heat is continued until gas ceases to be evolved, then the graduated tube (D) is so placed that the level of the liquid in it is the same as that in the outer vessel (B), and the volume of gas in (D) is read off. Supposing the sample of salt operated on to have been pure sodium monocarbonate, then no gas would be found in D; sodium sesquicarbonate would yield 272 c.c., and pure sodium bicarbonate 657 c.c. Scheibler's apparatus for determining the amount of carbonic acid is of like construction.

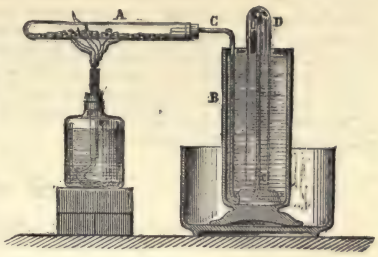


FIG. 164.

Uses.—Sodium bicarbonate is used in the preparation of pure sodium monocarbonate, for preparing alkaline baths of gold or platinum, from which these metals are deposited upon other metals in the form of a thin bright coating. A very considerable use is made of sodium bicarbonate for preparing effervescing beverages. Seidlitz powders consist of a mixture of five parts sodium bicarbonate and three parts tartaric acid. A method of preparing soda water consists in placing a previously prepared mixture of equal parts by weight sodium bicarbonate and tartaric acid in a strong bottle, filling up the bottle to about $\frac{4}{5}$ with water, rapidly closing it, and shaking up its contents. Since, by this method, sodium tartrate is dissolved in the soda water, which acts as a purgative, and has at the same time an unpleasant taste, other kinds of apparatus have been constructed by means of which carbonic acid alone is admitted into the water to be aerated. An apparatus of the kind is represented by figs. 165 and 168.

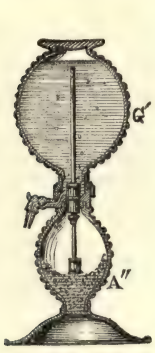


FIG. 165.



FIG. 166.



FIG. 167.



FIG. 168.

A mixture of 16·8 grams of sodium bicarbonate and 15 grams of tartaric acid are placed in a strong glass vessel (A), protected by a covering of wicker-work. The mouth of the bottle is then closed by the tube with the lid (D) fig. 167, the whole being then screwed upon a vessel (G) of 1 litre capacity, fig. 168, which is filled with water, and the apparatus inverted (fig. 165). Water passes through the tube (D) into

the lower vessel (A″), causing the sodium bicarbonate and tartaric acid to react upon one another. Carbonic acid is thereby liberated, and passes through the finely perforated plate (D′), fig. 167, into the upper vessel (G′), dissolving in the water contained in the latter. When soda water (or more properly aerated water) is required for use, the cock placed at the lowest part of (G) is opened, and the effervescing liquid drawn off. Of course all other liquids may be made effervescing in the above manner.

Other uses of sodium carbonate are for preserving milk, neutralising acid and beer, and for preparing the carbonic acid used in making Liebig's patent aerated bread. Sodium bicarbonate is also used in medicine, and for washing wool and silk, as well as many purposes in the laboratory.

SODIUM NITRATE.

FORMULA $NaNO_3$. MOLECULAR WEIGHT 85.

This salt, known as Chili saltpetre or cubic nitre, occurs abundantly in South America, forming, in the district of Tarapaca in Northern Chili, beds several feet thick, together with gypsum, common salt, sodium sulphate, etc. The crude salt is called caliche. The following table gives the composition of several samples of this material.

	Hayes				
Sodium nitrate . .	64·98	43·14	36·37	27·85	6·92
„ sulphate . .	3·00	26·30	11·67	43·20	0·68
„ chloride . .	28·69	11·40	44·80	18·30	88·70
„ iodide . .	0·63	—	—	—	—
Calcium sulphate .	—	1·36	1·36	0·68	—
Magnesium „ .	—	trace	trace	4·20	—
Insoluble substances .	2·70	10·30	3·30	0·32	0·03
Moisture . . .	—	7·05	2·50	6·00	3·50
	100·	100·	100·	100·55	99·83

The sodium nitrate is extracted by a rough lixiviation with hot water, separating impurities and allowing the clear concentrated solution to crystallise.

Characters.—Sodium nitrate crystallises in oblique rhombohedrons closely resembling cubes, and in this respect it differs from potassium nitrate which crystallises in prisms. The salt is slightly deliquescent and readily soluble in water, requiring little more than its own weight of cold water for solution; it melts at about 310° and forms a white mass on cooling. At a red heat it is decomposed in the same manner and more readily than potassium nitrate.

Uses.—Sodium nitrate is used chiefly for preparing nitric acid or for conversion into potassium nitrate, and as a manure.

SODIUM PHOSPHATE.

FORMULA Na_2HPO_4. MOLECULAR WEIGHT 142.

This salt is frequently termed neutral sodium phosphate, but its constitution is that of an acid salt; it is met with in commerce in a crystallised form, containing 12 molecules of water of crystallisation ($Na_2HPO_4 12aq$); it dissolves in 4 times its weight of cold water, and in less than its weight of boiling water; the solution has a faintly alkaline reaction; the crystals effloresce in contact with dry air; the taste of the salt is saline and cooling, and less unpleasant than that of sodium sulphate. When moderately heated the whole of the water of crystallisation is given off; at a red heat the basic hydrogen is given off in the form of water, and the salt is converted into neutral sodium pyrophosphate:

$$2Na_2HPO_4 - H_2O = Na_4P_2O_7.$$

Sodium phosphate is generally prepared by adding a solution of sodium carbonate to the acid calcium phosphate obtained by treating bones with sulphuric acid, as in the preparation of phosphorus, separating the precipitated calcium carbonate, and evaporating the clear solution sufficiently to obtain the salt in crystals.

There are two other sodium phosphates corresponding to ordinary tribasic phosphoric acid, but differing in the relative proportion of sodium and phosphorus from the salt above described; one containing three atomic proportions of sodium Na_3PO_4 is called trisodic phosphate, and the other containing two atomic proportions

of hydrogen with only one of sodium NaH_2PO_4 is called monosodic phosphate. The former is the neutral salt, inasmuch as the whole of the hydrogen of tribasic phosphoric acid is replaced by sodium, and the latter as well as the disodic salt ordinarily met with are acid salts.

When a solution of disodic phosphate is mixed with a solution of about half its weight of ammonium phosphate and evaporated to crystallisation, a salt is obtained which has a composition represented by the formula $NaNH_4HPO_4$ 4aq. and is termed microcosmic salt; it has a cooling taste, dissolves readily in water, melts when heated, giving off water and ammonia, until nothing remains but sodium metaphosphate, which has in a melted state the property of dissolving many metallic oxides, and thus forming characteristically coloured phosphates; on this account microcosmic salt is used as a flux in blowpipe experiments.

SODIUM BIBORATE (BORAX).

Formula $Na_2O2B_2O_3$. Molecular Weight 164.

History.—The first mention of borax is in the writings of the Arabian chemist Geber, and the alchemists of the thirteenth and fourteenth centuries seem to have been acquainted with the substance, but considered it a product of art. Its preparation and chemical constitution were not known until the middle of the eighteenth century, when, in 1747, Baron published his researches upon the substance.

Occurrence.—Borax occurs naturally in the water of certain inland seas, in China, India, Persia, California, and South America. The water of these seas when evaporated yields a crystalline residue, which has received the name of tincal, and is imported into Europe chiefly from China and India.

A compound of boracic acid with calcium and sodium has been discovered in Peru. It is a soft, light, whitish, scaly mass, and has the following composition:—

		Borocalcite (*Hayes*).	Boronatrocalcite (*Dick*).
Boracic acid	46·4	46·11	45·42
Water	32·6	35·00	97·42
Lime	14·0	18·81	14·32
Soda	5·2	—	9·63
Sodium chloride	1·8	—	—
Potash	—	—	0·51
Chlorine	—	—	1·10
Sulphuric acid	—	—	1·10
	100·0		

The substance is evidently a mixture of borocalcite and boronatrocalcite, of which Hayes and Dick have given the analyses as above.

Borax may be easily obtained from this compound by treating it with soda at a temperature of 100° C.

Characters.—Ordinary or prismatic borax is sodium biborate ($Na_2O2B_2O_3$ + $10H_2O$). It forms colourless transparent crystals, belonging to the rhombic system, the surface becoming efflorescent upon exposure to the atmosphere. Its specific gravity is 1·705. It is soluble in water, to which it imparts a weakly alkaline reaction. The solubility of borax in water increases with the temperature, as may be seen from the following table:—

Solubility of borax in 100 parts of water

At 0°	2·83	At 40°	17·90
„ 10°	4·65	„ 60°	40·43
„ 20°	7·83	„ 80°	76·19
„ 30°	11·00	„ 100°	201·43

Prismatic borax, when heated, melts in its water of crystallisation, which is given off, leaving a spongy mass known as burnt borax. The application of a stronger heat converts borax into a viscous glass—borax glass.

When an aqueous solution of borax, of specific gravity 1·245, is allowed to crystallise at a temperature of 79° to 56° C., regular octahedra are obtained, which contain only 5 equivalents of water. The octahedral borax differs from ordinary borax, not only in its crystalline form, but by its remaining clear when exposed to a dry atmo-

sphere, while ordinary borax effloresces superficially, owing to loss of water of crystallisation. On the other hand, octahedral borax disintegrates on the surface when exposed to a moist atmosphere, owing to its passing into the prismatic form; while ordinary borax, under the same conditions, remains pellucid. Octahedral borax is also harder than the prismatic variety, and its specific gravity is 1·815.

Melted borax possesses the property of dissolving metallic oxides with facility, its chief use being due to this property. Most metallic oxides impart to the borax glass a tint which is characteristic for the particular oxide. Thus, for instance, chromium oxide imparts a green tinge, cobalt oxide a blue colour, and manganous oxide an amethyst hue, etc. This solvent action of borax upon metallic oxides is due no doubt to the fact that a part of the boracic acid enters into combination with the metallic oxide, which then combines with the neutral sodium borate to form the double compounds.

The use of borax in soldering is also due to a similar chemical combination. It is necessary, in order to secure perfect soldering of two metals, that their surfaces should be free from oxide. This is effected by spreading over their surface a film of melted borax, which dissolves the metallic oxide and protects the naked surfaces of the two metals during the soldering process from the oxidising action of the air.

The use of borax in smelting depends upon its property of dissolving metallic oxides and converting them into a liquid slag.

Preparation.—Formerly the entire quantity of borax sent to the market was obtained from the water of certain lakes in Asia. The chief lake is the Teschu-Lumbu Sea in Thibet, the water of which contains considerable quantities of borax. Borax is now made from native calcium borate and from boracic acid.

From the water of the Borax lakes.—The water of these lakes is simply evaporated by the summer heat, leaving behind a crystalline mass, containing earthy, fatty, and other impurities, which is known in the market as tincal. This tincal or raw borax was formerly submitted to a process of crystallisation at Venice, and came into the market as Venetian borax.

California borax is obtained from the mud of a lake called Clear Lake, by drying it in the air, lixiviating with water and evaporating the lye till it crystallises.

From native Calcium Borate.—Borax has been obtained of late from the borocalcite and boronatrocalcite found in Peru, by boiling the finely powdered minerals for some time with a solution of soda, decanting the clear liquid from the insoluble calcium carbonate, and setting to crystallise.

Lunge, in treating boronatrocalcite for borax, separates out the specifically heavier gypsum by elutriation, treats with warm dilute hydrochloric acid, decants and crystallises, whereupon nearly all the boracic acid crystallises out.

From Boracic Acid.—The greater part of the borax which comes into the market at the present day is prepared from boracic acid obtained from Tuscany. This method was introduced in 1818 by Payen and Cartier.

A large tub, lined with lead, is charged with about 200 gallons of water, heated to 100° C. by means of a perforated steam coil lying at the bottom of the tub, and 20 cwt. of soda crystals. As soon as the soda is dissolved, 23½ cwts. of boracic acid are then added in small portions at a time. The addition of the boracic acid causes a strong effervescence, which is more violent towards the end, owing to the double and sesquicarbonates of sodium formed at the beginning being decomposed by the excess of boracic acid. On this account more caution is required in adding the last portions of boracic acid. The frothing of the mass ceases a few moments before the addition of the last portions of boracic acid, at which point the temperature of the liquid ought to be 104° C., and it ought to show a specific gravity of 1·160 to 1·170. If it is more concentrated than this, water is to be added. If, on the other hand, the concentration is not sufficient, raw borax is thrown in until the right specific gravity is attained. The lid of the tub, which is made of three pieces, is then put on, and the liquid, after having been allowed to stand from 10 to 12 hours to get clear, is decanted off with a siphon and run into the crystallising pans. These consist of large wooden vats lined with lead, about 20 feet long, 5½ feet wide, and 1 foot deep. A single vat of the kind is capable of holding the entire contents of the dissolving tub in which the boracic acid and soda are made to react. The mud which collects upon the bottom of the dissolving tub is let out by removing a plug at the bottom. This mud consists of sand, clay, calcium carbonate, and magnesium carbonate, produced by the action of soda upon gypsum and magnesium sulphate. The lye mechanically retained between the mud particles is washed out with water, and the wash water is used instead of fresh water for dissolving soda in a subsequent operation. The crystallisation of the borax is complete, according to the surrounding temperature, in 36–72 hours. The mother liquor is then drawn off by removing a plug at the bottom of the vessel, the handle of which extends above the surface of the lye. The crystalline mass is removed, and

placed upon an inclined plain, so as to drain off the mother liquor, which is collected in a reservoir. From this reservoir the mother liquor is once more brought into the dissolving tub, where it is mixed with the wash water from the muddy residue, and soda and boracic acid are then added in quantities sufficient to bring the concentration of the solution to sp. gr. 1·169. The whole is allowed to remain quiet for ten or twelve hours, and then the clear liquor is decanted off and crystallised. After three or four operations of this kind, according to the purity of the boracic acid employed, such quantities of sodium sulphate collect in the mother liquor, that upon cooling the latter down to 30°–31°C. this salt crystallises out.

On evaporating the mother liquor again in a cast-iron vessel, it yields a further crop of crystals of boracic acid, and the mother liquor from these gives a further crop of sodium sulphate. The mother liquor can be treated for common salt, and the final mother liquor evaporated to dryness: the saline mass thus obtained contains borax and may be used in the manufacture of glass.

The method employed in England consists in melting together in a muffle furnace under constant stirring a mixture of crude boracic acid with half its weight of calcined soda, the escaping vapours, which contain ammonium carbonate, being condensed in a suitable chamber. The melted product is lixiviated with hot water in iron boilers, the liquor allowed to clarify, then decanted and gradually cooled. The more gradual the cooling, the better are the crystals obtained. The precipitation from the solution of hydrated ferric oxide is effected by adding soda residue in the proportion of 1 pound for every two tons of lye. The clear lye is then crystallised.

Attempts have recently been made in France to obtain borax together with fuming sulphuric acid (vide page 113), by distilling together boracic acid and sodium sulphate, and treating the residue for borax.

It has been proposed to prepare borax in a similar manner, together with nitric acid, by heating to redness a mixture of Chili saltpetre and boracic acid.

Purification of Tincal.—Tincal was formerly purified by a process of washing. For this purpose it was placed in a cloth bag and agitated with a dilute solution of caustic soda as long as the filtrate ran away coloured. The washed mass was then dissolved in water containing a small quantity of soda, the liquor boiled up, then filtered and evaporated to crystallisation. The washing with caustic soda served to saponify and remove a fatty substance contained in the crude tincal.

Tincal may be purified by pouring over it, first of all, milk of lime, then boiling water, filtering, adding to the filtrate calcium chloride, and evaporating this filtrate to crystallisation. A calcium soap is thus formed, which remains behind upon filtering the solution.

Clouet's method consists in calcining powdered tincal, previously mixed with 10 per cent. of Chili saltpetre, in cast-iron pans, so as to destroy the fatty substance. The calcined mass is lixiviated and crystallised.

Tincal as well as artificially prepared raw borax admits of being purified in the following way. About 1,250 gallons of water contained in a tub lined with lead are brought to the boiling point by a steam-pipe immersed in the tub. In this water is hung a basket of wicker or wire work containing the raw borax, mixed with five per cent. of soda; the basket is so placed that it is entirely immersed, and fresh quantities of raw borax are dissolved in the water until the solution has a concentration corresponding to sp. gr. 1·169. When this point has been attained, the supply of steam is shut off, the liquid allowed to settle for two hours, the clear liquor is drawn off by cocks placed a little above the bottom of the tub into a crystallising vessel of lead surrounded with wood, about eight feet long, of a like breadth, and $4\frac{3}{4}$ feet deep. This is filled to within $1\frac{1}{4}$ to $1\frac{1}{2}$ in. of the brim, and is immediately covered with a wooden lid covered over with sheet lead, which serves, by condensing water on its surface, to produce a layer of water on the surface of the lye, and by this means to avoid the formation of small crystals at the surface. After a lapse of eighteen or twenty days, according to the surrounding temperature, the crystallisation is complete, and the temperature of the liquid reduced to 27° or 28° C. It is not advisable to wait longer than this, since impurities would be liable to find their way into the crystalline mass. The mother lye is drawn off, the last portions being rubbed off with a sponge, and the crystallising vessel immediately closed, so as to prevent the crystals from cracking. After a lapse of three hours the crystals are taken out and placed upon wooden tables to dry, and sorted and packed.

Preparation of Octahedral Borax.—This kind of borax is to be preferred in nearly every respect to the ordinary borax. It is harder, contains less water, froths less when heated, melts quicker, and adheres better to surfaces to be soldered together.

For preparing it, the apparatus used is that described for the preparation of ordinary borax, the only difference consisting in the proportions of water and borax.

Borax is dissolved in the way above described, until the solution shows a spec. grav. of 1·245. The liquor is then allowed to settle, drawn off when clear into crystallising vessels, and left there for five or eight days. As soon as the temperature has fallen to 79° C., the crystallisation begins, and is allowed to continue until the temperature has sunk to 56° C. If the crystallisation be allowed to continue at a lower temperature than this, a crystallisation of ordinary borax round the octahedral variety would take place. For this reason the lye is quickly drawn off by a number of siphons directly the temperature has sunk to 56° C. and the crystalline mass is removed. The mass requires protection from a moist atmosphere so as to prevent its attracting moisture and passing into ordinary borax.

Uses.—Borax is used in large quantities for soldering copper, silver, gold, etc.; in the preparation of certain kinds of glass enamels; in glass and porcelain paintings; in smelting works; in the detection of metallic oxides, with the blowpipe, etc. Borax is further used in hair washes; and in fixing of certain colours in calico-printing.

Besides borax there are some other borates which have been employed, such as those of zinc and manganese, used as siccatives in the preparation of varnishes; chromium borate is used for preparing Guignet's green; ammonium borate is used for rendering fabrics fire-proof, etc.

LITHIUM.

Symbol Li. Atomic Weight 7.

This metal was discovered in the state of oxide by Asfvedson, in 1817, as a constituent of petalite; it also occurs in spodumene, amblygonite, triphyline, lepidolite and other minerals, in several kinds of mineral water, in sea-water, and in some meteorites. It was first obtained in the metallic state by Bunsen.

Lithium has a slightly yellowish-white colour, is harder than sodium and has a specific gravity of 0·578, being the lightest solid substance known; it is less oxidisable than the other alkaline metals, melts at 180°, and takes fire at a higher temperature, burning with an intense white light; in contact with water it oxidises and displaces hydrogen, but does not melt like sodium.

The compounds of lithium closely resemble in general characters those of the other alkaline metals. The chloride crystallises in cubes, but is very deliquescent; the hydrate LiHO is much less soluble in water than potassium or sodium hydrates, and separates from the solution in small granular crystals, which melt readily below a red heat, corroding platinum, and solidifying on cooling to a crystalline mass; the carbonate Li_2CO_3 is only sparingly soluble in water; the phosphate Li_3PO_4 is also insoluble.

CÆSIUM AND RUBIDIUM.

Cs	Symbol	Rb
133	Atomic Weight	85·4

These two metals were discovered by Bunsen and Kirchhoff in 1860 and 1861. They are of frequent occurrence but always in very minute proportions, chiefly in minerals containing lithium and in some kinds of mineral water. They closely resemble potassium, both in their general physical and chemical characters.

CALCIUM.

Symbol Ca. Atomic Weight 40.

Although the discovery of the metals potassium and sodium, and the analogy between the alkalies and alkaline earths, suggested the probability that the latter were also oxides of metals, calcium was not isolated in a pure state until some few years since by Mathiessen; it is a yellowish coloured metal that melts at a red heat, is very malleable, oxidises readily when exposed to moist air, and decomposes in water. Calcium is divalent and its compounds possess the characters of salts.

Occurrence.—Calcium occurs very abundantly in various states of combination; the fluoride occurs as fluor spar, the carbonate in the several forms of calc spar, arragonite, limestone, chalk, etc., and combined with magnesium carbonate as dolomite. Several silicates occur as wollastonite, etc., as well as in combination with other silicates. Calcium also occurs combined with silicic acid in a great number of minerals, and the hardening of cements and hydraulic lime is due to the presence of calcium silicate.

Other compounds of calcium that occur very frequently and abundantly are, gypsum, $CaSO_4 + 2H_2O$; Anhydrite, $CaSO_4$; Apatite, $Ca_3P_2O_5 + CaCl_2$ or CaF_2; Calcium nitrate, $Ca2NO_3$; Fluor spar, CaF_2.

Compounds of calcium occur abundantly in both the vegetable and animal kingdom; the ashes of plants contain both the sulphate and the carbonate; corals, oyster shells, and eggs consist essentially of calcium carbonate, and bones consist of calcium carbonate and calcium phosphate.

CALCIUM OXIDE (LIME).

Formula CaO. Molecular Weight 56.

Occurrence.—Lime does not occur naturally; but, in combination with carbonic dioxide and other acid oxides, it forms a very large portion of the earth's crust.

Characters.—Calcium oxide or 'quick' lime is a white, hard, amorphous mass, which has a specific gravity of 2·300. It cannot be melted even by the heat of the oxyhydrogen flame, but becomes intensely luminous when thus heated. The Drummond light used for signalling is produced in this way.

Lime combines readily with water, and when exposed to the air gradually absorbs water and carbonic acid, and is thereby rendered useless, on which account it must either be used shortly after burning, or must be preserved from contact with moisture and the action of the air.

Preparation.—Lime, or crude calcium oxide, is prepared by strongly heating any of the various natural calcium carbonates, and the operation is technically termed lime burning. Intense heat causes the decomposition of calcium carbonate into calcium oxide, or lime, and carbonic acid which escapes in the gaseous condition:

$$CaCO_3 = CaO + CO_2.$$

One hundred parts of calcium carbonate should yield 56 parts of lime; but this result is seldom obtained in preparing lime on a large scale, owing to the presence of foreign ingredients in crude limestone.

By calcining ordinary limestone, which is generally somewhat impure, lime is obtained containing small quantities of ferric oxide, magnesia, clay, etc., which weaken its resistance to the action of fire as well as its capacity for combining with water.

The material selected for preparing lime should be of tolerable purity, and it should not contain more than from 2 to 5 per cent. of impurities, since, as above mentioned, the quality of the lime depends very much upon the amount of foreign substances. Lime is also better in quality, the harder the limestone is from which it is

prepared, on which account marble is the substance most suited for preparing lime. Marble is, however, as a rule too dear for the purpose, and the material generally used is ordinary limestone; calcareous marl, or shells, etc., being seldom employed. Chalk is often used for preparing lime, and owing to its porous nature it decomposes in burning far more easily than ordinary limestone.

The operation of lime burning is carried out in heaps, field kilns, pits, or in specially constructed kilns.

Burning in Heaps.—The pieces of limestone are either arranged alternately between layers of fuel, or the entire quantity of limestone is laid upon a thick bed of fuel and the whole covered, as in preparing charcoal, with earth, clods, etc. The operation is conducted throughout in a way similar to that adopted in making charcoal.

Burning in Field Ovens.—In this plan the larger pieces of limestone are built up so as to form a fire chamber, and the small pieces of limestone piled up over them.

Burning in Pits.—For this purpose pits dug in the ground are either filled with alternate layers of limestone and fuel, or the limestone is arranged so as to form an arch under which the fuel is burnt.

Burning in Kilns.—Lime kilns are of two kinds, those in which the burning is interrupted, and those in which the burning is continuous.

Periodic Kilns.—Kilns of this kind are much used and are convenient in places where the consumption of lime is irregular, since, as we have seen, a lime that has been long burnt is not so good as that which has been recently burnt.

The kilns are made of fire brick, and have either a cylindrical or an oval form, being furnished below with a large heating hole. The kilns are charged by piling up large pieces of limestone upon the hearth of the kiln so as to form an arch, which is then covered over with small pieces of limestone until the kiln is full; care being always taken to secure a free space for the fire. Some easily combustible fuel is then introduced through the stoke-hole beneath the arch and ignited, by which means the limestone is gradually heated. A gradual heating is necessary at first in order to prevent the limestone forming the arch from crumbling and falling into the fire space. The lighter kind of fuel is then replaced by fuel of a denser kind, and the heat increased until the pieces of limestone at the mouth of the furnace are white hot; the burnt lime is allowed to cool a little, withdrawn, and the kiln recharged.

Kilns of a similar kind are employed in which the hearth is formed of a grate and ash pit; the pieces of limestone, as in the above case, are built up so as to form an arch, the only difference being that the fuel is burnt on the grate.

A very useful periodic kiln with grate is shown in fig. 169. The shaft (A) is 11½ feet wide below, and 10 feet wide at its upper extremity; it has a height of 11 feet, and is covered above with an arch (*b*) furnished with draught holes; *d d* are firing holes each of which has a fire grate inclined towards the hearth of the furnace upon which the fuel is laid; *g* is an opening for admitting the limestone. The latter, as well as the opening (*h*) for drawing out the lime, are walled in during the burning;

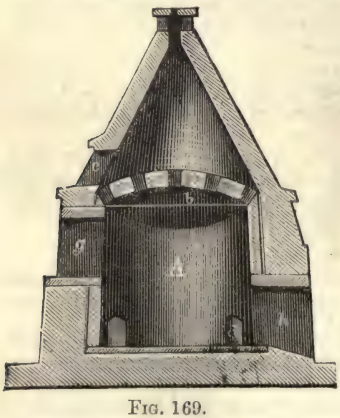


Fig. 169.

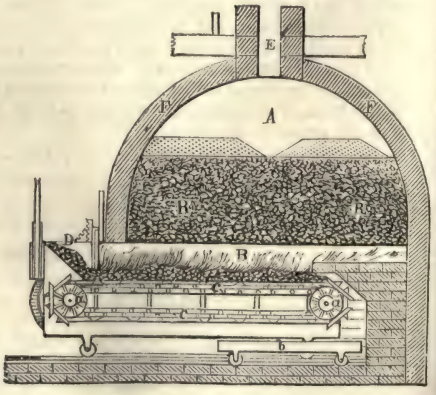


Fig. 170.

c is an aperture in the hood covering the furnace through which the draught holes may be observed, and the heat regulated or directed to any desired part of the furnace by placing bricks over the draught holes.

For charging the furnace, a wooden pole is placed in a vertical position in the middle of the hearth, and the pieces of limestone arranged round it. The wooden stake or pole upon burning leaves a cylindrical hollow space which serves for the regulation of the combustion. The pieces of limestone are so arranged that, before and above each stoke hole, a free arched space is formed, where the fire gases collect and are distributed equally in all directions. During the first six hours a moderate fire only is kept up, the heat being gradually increased until yellow lime flames are observed at the upper opening of the furnace, and the contents of the kiln are uniformly heated to a sufficient degree. The time occupied by the operation is seventy-two hours.

Fig. 170 represents a kiln of novel construction by Swann, in which 20 per cent. less fuel is required than in ordinary kilns. A is a chamber of the kiln formed by the arch (F F), B the fireplace, furnished with an endless iron grate (*c c*), revolving upon the rollers (*a a*). D is a funnel for admitting the coal, E a flue through which the hot gases pass into the chimney; *b* is a small truck for reception and removal of the ash and coke falling from the hinder part of the moveable grate.

In working the kiln it is first charged with pieces of limestone (R R), and heated with hot air from other kilns; the fire then is ignited and fuel thrown in through the hopper (D); by means of the travelling endless hearth (*c*) the fuel is passed along the fire grate at such a rate that it is completely burnt by the time the part of the grate it falls upon gets to the other end of the fire. The air draught and fuel supply are regulated by means of sliding dampers in front of the furnace.

A number of kilns of this kind are placed together in such a way that the hot air can be made to pass from one kiln to the other. Fig. 171 represents a horizontal

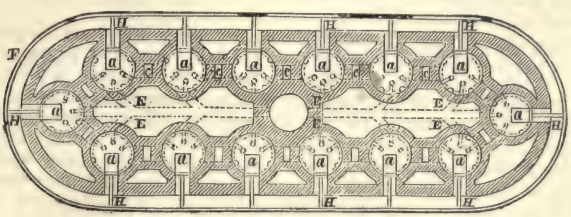


Fig. 171.

section of a system of the kind, where a number of Swann's furnaces are grouped together; *a a* are the individual kilns communicating with one another by means of the flues (*c c*), which open in the arch of one furnace, and terminate at the hearth of the next one. These flues admit of being closed by a sliding damper, which remains closed during the drying of the furnace, and is opened after that operation is over so as to admit the hot air into the next furnace. During the preliminary heating or drying process the hot gases escape through the flues (E E) into the chimney; F is a pipe in which hot air circulates and is conducted through the branch pipes (H H) into the fire-places. The method of heating this air is the same as in the blast furnaces of iron works.

Continuous Lime Kilns are variously constructed. Figs. 172 and 173 represent a kiln of the kind. It is funnel shaped at the upper part (*a b c d*) and cylindrical shaped at the lower part, below the line C D. Its greatest diameter at *a b* is 13 feet, its least diameter at *c d* only 5½ feet; its depth down to *c d* is about 13 feet. The arches (D, D′, D″) give access to the interior of the kiln for drawing the burnt lime, and they are at the lowest part 26 inches, and at the highest part about 8½ feet high. The apertures for drawing the lime are 20 inches high, 16 inches wide, and they are divided by pillars into two equal halves. The hearth of the furnace is furnished with a cone 32 inches high having at its base a diameter of 30 inches; the flue (*e f g h i k*) is for carrying off the gases evolved, so as to facilitate the working. Dry coal or coke is used as fuel. The limestone is broken into pieces about 1½ inches thick and 3 to 5 inches in breadth and length.

In working this kiln a small quantity of dry wood is placed upon the hearth, with about 11 bushels of coal, and above that 8 bushels of broken limestone. Alternate layers of 1 to 1½ inches of coal, and of limestone, 6 inches thick, are then put in until the kiln is quite full, and then the wood upon the hearth is set fire to. In proportion as the fuel burns, the calcined lime sinks down and is drawn out through the holes at the bottom of the kiln; fresh limestone and fuel being at the same time put in above. If, upon drawing out the lime, it should be insufficiently or too much burnt, the proportion of fuel added in charging the kiln is increased or

diminished. A kiln of this kind is capable of producing about 300 bushels of burnt lime in twenty-four hours with 120 bushels of coal.

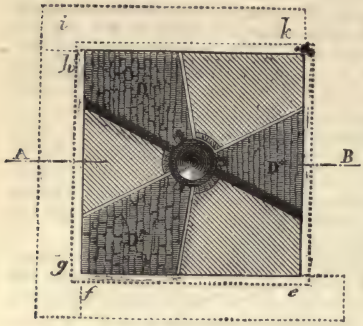


FIG. 172.

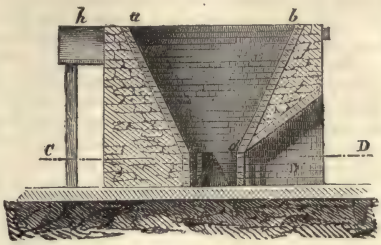


FIG. 173.

The working capability of this kiln is considerably increased by carrying it up in cylindrical form to a height of 3½ feet above *a b*, and to a height of 10 feet above that, with a gradual contraction to an opening 10 feet wide. A kiln of this kind yields 2500 bushels of burnt lime daily.

Continuous Lime Kilns with Lateral Furnaces.—These kilns have the advantage that the lime is not contaminated with ash from the fuel. Fig. 174 represents a kiln of the kind. The height of the shaft from the hearth to the mouth is 20 to 40 feet, its greatest diameter 5 to 10 feet. A is the fireplace with inclined grate, upon which wood, turf, or coal is burnt. The hot air from the fire passes through the flue (B) into the flue (*c'*), extending horizontally round the kiln, and through three openings (c) equidistant from one another, into the kiln. The height of these openings above the hearth of the kiln is 5 to 6½ feet. These kilns are sometimes furnished with three fireplaces, and the same number of stoke-holes. D is an opening for drawing out the lime, EE is a kind of hood for regulating the draught, and G a door for charging the kiln. In working this kiln it is first heated from below; the lateral fires are not lighted until afterwards.

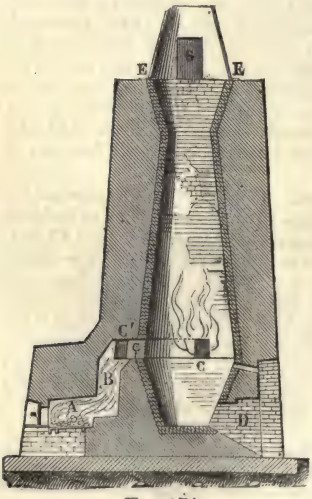


FIG. 174.

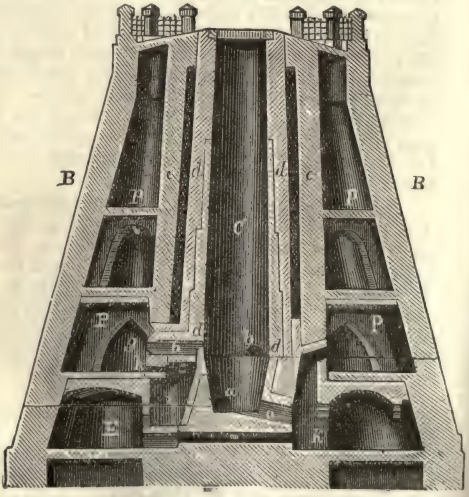


FIG. 175.

A kiln first used at Rüdersdorf, near Berlin, and now extensively employed, is represented by fig. 175. The lining (*d*) of the shaft consists of fire brick, and is surrounded by a counter wall (*e*), separated from the lining by ashes or some other bad conductor

of heat. The height of the kiln from the hearth to the mouth is about 38 feet, its greatest diameter 9 feet; the mouth is 6 feet wide, and the lower part 6½ feet wide. About 12 feet above the hearth of the shaft are the furnaces (*b b*), by which the kiln is heated, of which there are three in a kiln of the above dimensions, and four or five in larger kilns. The opening (*g*) of the furnace is closed by a door, and air passes under the grate at (*h*), from the ash-pit (*i*), which is so placed that the ashes are raked into the arched chamber (E). The kiln is enclosed by an outer wall (B B); and the gases from the kiln pass through the flue (K) into the chamber (F). The burnt lime is drawn out through a hole (*a a*) that can be closed by an iron door. This kiln, like the former, is first heated at the discharge aperture, and afterwards by means of the furnaces (*b b*). A kiln of the kind with three fireplaces yields a daily produce of 3 to 4 tons of burnt lime.

Lime Kilns heated by Gas have been only recently introduced. Steinmann has constructed a kiln of the kind in which the gas is generated in special generators beneath the shaft of the kiln, and having been deprived of tar vapour in a suitable chamber, is at once passed into the kiln. This kind of kiln is said to be especially adapted for sugar works, since both lime and carbonic acid can be obtained of great purity.

Lime is said to be dead burnt when it has been too strongly heated, and with the silica, alumina, etc. it contains made to undergo a kind of partial fusion. When insufficiently burnt the interior of the lumps still consists of carbonate. Both dead-burnt and half-burnt lime are useless for the ordinary purposes to which lime is applied.

The accompanying table gives the results of analyses of fat and meagre limestones, as well as the burnt lime obtained from them :

	Fat Limestone				Vichy (Allier)	Paris	Villefranche (Aveyron)
	Château Landon (S. et M.)	St. Jaques (Jura)	Craie de Paris	Lagueux near Lyons			
Limestone employed :							
Calcium carbonate .	97	96·5	98·5	94·5	87·2	74·5	60·7
Magnesium carbonate	2	2	—	1·6	10	24·3	30·3
Clay and iron oxide	1	1·5	1·5	3·9	2·8	1·2	3
Manganous carbonate	—	—	—	—	—	—	6
Burnt lime obtained :							
Lime . . .	96·4	95·4	97·2	91·6	86	78	60
Magnesia . .	1·8	1·8	—	1·5	9	20	26·2
Clay, iron oxide, and manganese oxide .	1·8	2·8	2·8	6·9	5	2	13·8

Uses.—The chief use of lime is for preparing mortar, by mixing 1 vol. slaked lime (containing about 70 per cent. of water) and 2 vols. sand with water, until they form a stiff paste. The hardening of mortar takes place in two ways—first, a partial drying and contraction without acquiring any great solidity, and then by the combination with carbonic acid and the conversion of caustic lime into calcium carbonate. After a considerable lapse of time, calcium silicate may also be formed in some cases, the silica being derived from the sand.

Lime is also used in the preparation of caustic alkalies and ammonia, in soap boiling, for precipitating magnesia from brine liquors, in the preparation of bleaching powder, potassium chlorate, certain disinfecting powders, for clearing solutions of soda, for removing carbonic acid from mineral waters and precipitation of calcium carbonate retained in solution by the carbonic acid. Considerable quantities of lime are used in preparing hydraulic mortar, for purifying illuminating gas from carbonic acid and sulphuretted hydrogen, by Laming's process. Lime is also used for decomposing Glauber's salt in the manufacture of soda, for bleaching some kinds of tissues, for purifying the air in pits, wells, cellars, etc. which contain dangerous gases, such as carbonic acid, sulphuretted hydrogen, etc.; in preparing indigo, in the dressing of corn, and in the manufacture of sugar. Lime is further extensively employed in the manufacture of glass, in treating raw pyroligneous acid for wood spirit, and acetic acid, in the preparation of alum from cryolite, in the manufacture of stearic acid, as an admixture for forming slag in blast furnaces and other metallurgical processes, for removing hair from the skin in tanning, for producing the

Drummond light, in the preparation of a large number of organic substances (citric, tartaric acids, etc.); for purifying camphor, for preserving eggs, fruit, etc.; in the preparation of absolute alcohol, in the manufacture of a number of lutings, as paint; for removing mould and acids from fermenting vats, etc.

CALCIUM HYDRATE.

FORMULA CaH_2O_2. MOLECULAR WEIGHT 74.

Calcium oxide combines with water at the ordinary temperature, forming the hydrate, great heat being evolved in the combination. This process is technically known as slaking. Upon mixing 2 parts of pure lime with 1 part water, the temperature of the mixture rises to 300°. The calcium hydrate or slaked lime thus formed is a light, white powder, occupying about 3 times as great a volume as the lime from which it was produced. Water dissolves at the ordinary temperature 14 per cent. of this calcium hydrate, while boiling water dissolves only about one-half that quantity. Upon evaporating aqueous solutions of calcium hydrate (lime water), the hydrate is obtained in the crystalline state.

Calcium hydrate rapidly absorbs carbonic dioxide from the atmosphere, forming calcium carbonate. When a somewhat thick mixture of lime and water is exposed to the air it gradually hardens, owing to the absorption of carbonic acid; to this cause is due the hardening of mortar.

CALCIUM CARBONATE.

FORMULA $CaCO_3$. MOLECULAR WEIGHT 100.

Occurrence.—Calcium carbonate occurs very abundantly in a great variety of forms. In a pure state, as calc spar, it is a colourless transparent mineral, but is often coloured, owing to the presence of iron manganese, etc.; it forms crystals belonging to the rhombohedral system.

Aragonite is another form of calcium carbonate, crystallising in rhombic prisms.

Calcium carbonate also occurs combined with magnesium carbonate as dolomite, $CaMg2CO_3$, crystallising in rhombohedra; when pure it is colourless, but more frequently it is of a yellow, grey, green, or brown colour, owing to the presence of iron, etc. Entire mountain ranges consist of dolomite.

Marble, limestone, and chalk all consist of calcium carbonate, in a more or less pure state; they often constitute entire mountain ranges. Marble has a crystalline structure, and when pure is perfectly white; but it is often coloured by admixtures of various metallic oxides, as well as organic substances. It occurs in layers in gneiss, micaceous schist, clay slate, and other rocks. Marble of an especially beautiful kind is found at Carrara and Serravezza in Italy. Chalk is a less pure calcium carbonate than marble; it occurs in England, North France, Denmark, etc., often constituting extensive strata. Ordinary limestone is a hard, opaque mass, often crystalline; it occurs as extensive beds. Its colour depends upon its mode of occurrence, either smoky grey, yellow, brown, or black. It nearly always contains a small quantity of magnesium carbonate and clay. Marly limestone is the name for a variety of limestone very rich in clay, etc. The stone used for lithographic purposes is a kind of schistous limestone occurring in Bavaria. Stalactites and stalagmites likewise consist of calcium carbonate. They owe their formation to calcareous water impregnated with carbonic acid dropping slowly from the roofs of caverns, and losing the greater portion of its carbonic acid upon coming into contact with the air, which causes a gradual deposition of calcium monocarbonate. Depositions of calcium monocarbonate are in like manner formed round springs, in water pipes, etc.

Characters.—Calcium carbonate is a colourless tasteless substance very sparingly soluble in water, requiring, according to Fresenius, 10,601 times its weight of cold water; the solution has a slightly alkaline reaction upon test paper. As prepared artificially calcium carbonate has the form of a white powder, but the particles generally have the crystalline form of calc spar. Calcium carbonate is decomposed at a dull red heat and readily gives off its carbonic dioxide, especially when heated in a current of air, by which the disengaged carbonic dioxide is removed.

Uses.—Calcium carbonate is used for a great number of purposes in chemical operations as well as for preparing lime.

CALCIUM FLUORIDE.

FORMULA CaF_2. MOLECULAR WEIGHT 78.

This substance occurs abundantly as fluor spar, and is chiefly important as a source of hydrofluoric acid. It is also used in some cases as a flux in smelting operations.

CALCIUM SULPHATE.

FORMULA $CaSO_4$. MOLECULAR WEIGHT 136.

Occurrence.—Anhydrous calcium sulphate occurs as anhydrite, sometimes in the state of crystals, but chiefly as a coarse compact mass.

In the hydrated condition calcium sulphate occurs as gypsum, in great abundance, especially accompanied by common salt. It is sometimes found in colourless crystals belonging to the monoclinic system; sometimes also in large crystals which consist of very thin laminæ, in which form it is known as selenite; it also occurs as a granular, crystalline, and translucent mass known as alabaster; more often in coarse crystalline masses as gypsum, either in the ordinary granular condition, or as fibrous gypsum. The occurrence of calcium sulphate dissolved in water has already been mentioned in treating of water.

Characters.—Calcium sulphate is sparingly soluble in water, 100 parts of water dissolving only 0·205 parts of gypsum at 0°, 0·237 parts at 12°, 0·254 parts at 35°, 0·251 parts at 50°, or 0·217 parts at 100°. The solubility is therefore greatest at a temperature of 35°.

Calcium sulphate is more readily soluble in dilute nitric or hydrochloric acid, and concentrated sulphuric acid dissolves considerable quantities. The solubility is increased by solutions of sodium chloride, potassium chloride, sal ammoniac, etc.

Gypsum when heated to 100° first of all gives up 15 per cent. of its water; but in order to drive off all the water, it must be heated to 170°. Gypsum deprived of its water by heating is termed burnt gypsum, or Plaster of Paris; and it possesses the property of hardening when mixed with water, the process being accompanied by the evolution of a considerable quantity of heat. Gypsum is said to be dead burnt when it has been heated so much that it has become slagged at the surface, and in this condition it is destitute of the power of combining with water, like the natural anhydrous calcium sulphate, anhydrite.

The hardening of burnt gypsum when treated with water is due to combination with water; 1 molecule of burnt gypsum combining with 2 molecules of water; if an excess of water be taken, it remains simply mechanically mixed in the crystals of hydrated calcium sulphate.

The hardness of the hydrated mass after treatment with water depends in part upon the proportion of water taken, and in part upon the constitution of the gypsum before burning. The best plaster of Paris is yielded by gypsum consisting of individual, dense, granular crystals, containing only a very small amount of calcium carbonate, and but a trace of clay.

Good gypsum properly burnt absorbs about its own volume of water, and forms a hard mass, the absorption being accompanied by a slight elevation of temperature. Plaster of Paris prepared from compact, fibrous, or laminated gypsum, absorbs much more water, but the product is less hard. The cause of this different behaviour is that very finely divided burnt gypsum becomes hydrated throughout its entire mass, and expands so that the particles are less closely aggregated, while the plaster of Paris made from granular gypsum retains its structure after burning, and when treated with water becomes hydrated only at the surface of the individual granules in the first instance, further absorption of water taking place slowly afterwards and without so much expansion of the mass.

When plaster of Paris that has been slaked and become hard is reduced to powder and again mixed with water, it sets again after a short time, but the product is not so hard as before. This operation may be repeated four or five times when the gypsum is of good quality, and, indeed, it is a simple means of determining the quality of plaster of Paris. A good sample may be treated in this way five times with an equal volume of water without entirely losing the power of setting.

From the property possessed by plaster of Paris of absorbing water with great avidity, it is obvious that it requires keeping out of contact with moist air.

Preparation.—The burning of ordinary gypsum was formerly carried out in kilns having a construction represented by fig. 176, being formed of three walls covered with a roof of wood or iron covered with tiles. Large pieces of gypsum are piled up in this chamber so as to form a series of arches, each arch having an aperture of 12 to 18 inches, and the smaller pieces of gypsum are heaped abovet he arches.

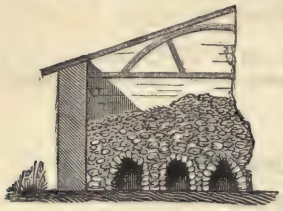
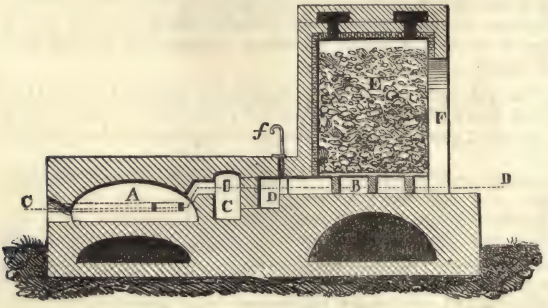


Fig. 176.

Dry wood is used as fuel, brushwood being the best. The flame penetrates the spaces between the pieces of gypsum, and after a time the heap is covered over with more small pieces of gypsum. After ten to twelve hours, if the gypsum be sufficiently burnt, the supply of fuel is stopped and the mass covered over with refuse gypsum dust, which becomes partly burnt and thus increases the yield. After being allowed to cool for about five or six hours, the arches are broken down, the lumps broken into pieces, and packed in sacks for the market.

This method of burning gypsum is of course very imperfect, Upon examining the lumps, it is found that the surface is dead burnt, while the interior is hardly sufficiently burnt. Where these kilns are used the chief thing to be attended to is that the proportion of unburnt and dead-burnt lumps is relatively slight, so that the total product is sufficiently plastic.

Fig. 177.



Shaft kilns are sometimes used for burning gypsum. They differ in construction and yield far better results than the kilns above mentioned. These kilns are either worked continuously or intermittently.

The continuous shaft kilns are comparatively seldom used, owing to their requiring considerable attention. They may have a construction similar to the lime kilns (figs. 172 and 173, p. 284).

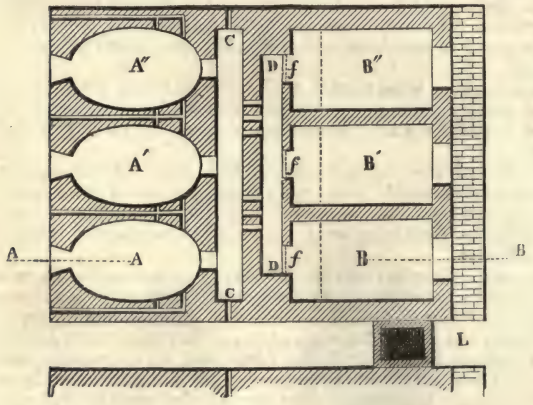


Fig. 178.

The intermittent kilns are employed in a number of districts; they have either a form such as shown in fig. 178, or are of a cubical form with rounded edges, cylindrical, etc. They are charged by first of all building upon the hearth large pieces of gypsum, so as to form two fire channels serving the purpose of igniting the kiln through the stoke holes, and then the kiln is filled by piling up alternate layers of fuel and stones. In some places, after being charged in the above way, the heaping up of alternate layers of fuel and stones is continued until a stack 12 feet high protrudes above the mouth of the furnace. The kilns are set going by making a fire upon the grate, which is kept up for a day or a day and a half. By means of the fire channels the combustion is propagated to the upper layers of fuel, and the whole mass is thus ignited. When the burning is over, the fire channels are broken down, and the whole allowed to cool, so as to fit it for removal.

Gypsum kilns are sometimes heated by the hot air from coke ovens, since gypsum burning does not require a very high temperature, and advantage is taken in some cases of the waste heat escaping from coke ovens. Figs. 177 and 178 represent an arrangement of the kind. A A′ A″ are the coke ovens from which the hot air is conducted into the common flue (C), whence it passes through (D) and the openings (*f*) into the chambers (B B′ B″) under the grates of the gypsum kilns (B). The hot air passes through the gypsum mass and is conducted together with the steam escaping from the gypsum into flues above the ovens, escaping finally into the common chimney (L). F is an opening for charging and emptying.

Dumesnil's gypsum kiln is shown in section in fig. 179. A brickwork foundation; B fireplace beneath the hearth; *b′* channel for admitting the fuel; *b″* opening for draught and withdrawal of ash; *c c* 6 to 8 channels for conducting the hot air from the fireplace (B) into the combustion chamber (D). These channels terminate at the hearth in a corresponding number of cast-iron mouth-pieces (*i*, figs. 180 and 181),



Fig. 180.



Fig. 181.

Fig. 179.

furnished with about twenty or thirty lateral slits, through which the hot air passes into the combustion chamber; *f* is an opening for admitting the first charge of stones as well as for emptying the furnace; *f′* is an opening through which the filling is completed; *g g* are small channels kept open at the beginning of the operation so as to allow of the escape of the large quantities of steam evolved, but these openings are finally closed towards the end of the operation, the chief chimney then serving for conducting off the steam.

The pieces of gypsum having an average diameter of 4 or 5 inches are set up vertically in the kiln; the larger ones being placed at the bottom, and the smaller pieces piled upon them.

Gypsum prepared according to the methods above described is, however, not suited for fine castings; a very white and plastic gypsum being required for such purposes. In preparing the better kinds of plaster of Paris, great care must be taken to secure uniform burning of the gypsum, and the admixture of ash from the fuel employed must be avoided.

In burning gypsum required for artistic purposes, it is often reduced to a fine powder and heated very carefully in metallic cauldrons, or in cast-iron cylinders provided with stirrers.

Plaster of Paris of good quality is sometimes prepared by burning homogeneous pieces of gypsum upon the hearth of an ordinary baking oven. The oven is first of all heated to redness, the fuel and ash then withdrawn, and the pieces of gypsum laid

upon the hearth. The gypsum for this purpose ought to be of a granular crystalline nature, and not of very dense structure. According to this method no dead-burnt gypsum can be formed, since the oven is not too hot, and its temperature is much reduced by the cold gypsum. The lumps are left in the oven until a portion upon being taken out and tested is found to have been burnt through.

Hardening of Gypsum.—Many kinds of gypsum, when burnt and slaked, yield a very soft product, and even gypsum of the best quality may be easily scratched. It is only recently that a method has been discovered for preparing a harder and at the same time less soluble gypsum. The operation consists in burning pieces of gypsum about the size of a fist in suitable kilns at a scarcely perceptible red heat. After burning the gypsum it is placed in a solution of alum, containing 12 per cent. of the salt, at a temperature of 35°. After the lapse of two or three hours, the gypsum is taken out, drained, and dried at a gentle heat, and again submitted to a burning process, as before. The gypsum that has been thus twice burnt is powdered and sifted. When required for use, it is either mixed with water, or still better with a solution of alum, containing 7 to 8 per cent. of the salt. To form a proper paste only 55 to 57 per cent. of liquid is required, while ordinarily good plaster of Paris requires 67 to 100 per cent. of water. But while the plaster containing alum requires fifty-five to sixty minutes to harden, that without sets in about fifteen or seventeen minutes; it has, however, the great advantage over ordinary plaster of being very much harder; indeed it is almost as hard as marble, and may be struck moderately, with a hammer, without being injured. The mass when struck gives a ringing sound. Alumed plaster is further only very slightly soluble in water, so that casts made of it may be washed without injury.

This effect of alum upon gypsum has not at present been explained; it is, however, probably due to the formation of a double salt of potassium and calcium sulphate.

The use of other salts in place of alum for hardening gypsum has been tried, but without success—such as borax, soluble potassium silicate, potassium carbonate, seignette salt, etc.

For the superficial hardening of gypsum casts Knaur and Knop recommend washing them with a mixture of potash water-glass solution, and a solution of curdled milk in caustic potash. Objects thus treated may be washed without danger.

Uses.—Gypsum is seldom employed in an unburnt condition, except as a building stone, which is of little durability, owing to the solubility of gypsum in water. Alabaster is used for making vases, table slabs, etc. Gypsum powder is used for decomposing ammonium carbonate in the preparation of ammonium sulphate. As a manure, burnt gypsum is preferable, owing to the greater facility with which it can be reduced to powder. Natural gypsum is further extensively used for mixing with colours, etc. Anhydrite is used for making vases, mouldings, etc.

Plaster of Paris is very extensively used as a cement, and for making mouldings, ceilings, and various ornaments, etc. No other substance can be so cheaply and quickly used for casting and luting. Plates furnished with grooves and pins are cast from gypsum; they are used for dry partition walls, for which purpose old mortar, coal ash, broken pieces of crockery, bricks, etc. may be added to the gypsum so as to render the mass cheaper. Dumesnil prepares useful bricks in the following way: 7 parts by weight of alum are mixed with 6 parts of lime flour, and 1 part of yellow ochre, the whole being stirred up with 500 parts by weight of water and 1 part of glue dissolved in five parts of warm water added. This mixture is then poured over 900 parts of gypsum, 450 parts of river sand being added at the same time. The paste obtained is cast into moulds and dried when set. In order to secure the bricks against the solvent action of rain water, they are painted over three times with a solution of potash water-glass of specific gravity 1·15 to 1·20.

A very common application of gypsum is for casting all kinds of medals, statues, busts, etc. Gypsum moulds serve for casting in gypsum as well as in metal, also for preparing galvanoplastic reliefs, and busts, etc., for which purpose the gypsum mould is saturated with a mixture of resin and wax, and its surface rubbed over with graphite or silver, so as to render it conductive.

Gypsum marble, or stucco, used for walls, pillars, etc., is prepared by applying a mixture of fine plaster with glue water upon a coarse gypsum ground, and when dry the surface is polished with pumice stone. The pores still remaining in the substance are filled up with a paste made by mixing gypsum with glue water, and after drying the whole is painted over with a very thin paste of the same kind; after the second drying the work is polished with tripoli powder, rubbed over it with a linen cushion; it is then smeared with oil, and receives a final polish with tripoli and oil. Stucco is coloured according to pleasure, by mixing the glue water with which the gypsum is stirred up with red lead, indigo, amber, lamp black, etc.

Plaster casts are prepared by heating them to about 88° and then dipping them into melted stearin or paraffin. When cool polish is given by brushing.

Gypsum moulds, owing to their porosity, are often used for moulding objects in porcelain, etc. The moulds absorb water, and thus the porcelain mass is dried and hardened. Owing to its absorbent nature gypsum is also used for drying colours, yeast, etc. Gypsum forms a good luting for glass bottles with glass stoppers. For joining broken busts or casts of gypsum, a cement is employed consisting of gypsum stirred up with a solution of alum or gum.

Gypsum is very extensively used for agricultural purposes, and it exerts a very beneficial effect upon leguminous, liliaceous, and other plants. Gypsum burnt and slaked in the air, strewed upon the soil in wet weather, exerts a beneficial effect, partly by virtue of its own constituents, and partly by fixing ammonia and ammonium salts from air and rain water, and also partly by its decomposing magnesium and potassium salts. From 1 cwt. to 5 cwt. of gypsum are used for every acre of soil. Gypsum is also used as a manure by mixing it with urine, in which case its effect is due to the conversion of ammonia into non-volatile ammonium sulphate.

Light white wines are mixed with ·2 or ·3 per cent of gypsum, so as to retard fermentation and prevent acidity. Gypsum is also used for rendering weak wines stronger by absorbing some of the water, and thus increasing the relative amount of alcohol.

Hardened gypsum is also used for casts, busts, etc. It is more suited for painting upon than ordinary gypsum, owing to its greater density and less absorbing power.

Two preparations are found in the market, the one known as pearl hardening, the other under the name of annalin, both of which are used as an addition to paper pulp in the manufacture of paper. Annalin consists essentially of gypsum, and is obtained in this country as a by-product in the preparation of carbonic acid. The calcium chloride residue obtained by the action of hydrochloric acid upon chalk is precipitated with sulphuric acid, the gypsum filtered upon a woollen cloth, washed with dilute lime water, and then pressed in linen pressing cloths. The cakes thus obtained are sent into the market; they contain about 40 per cent. of water.

CALCIUM PHOSPHATE.

FORMULA $Ca_3P_2O_8$. MOLECULAR WEIGHT 310.

The salt occurs in bones, and is therefore commonly called bone phosphate; it also occurs naturally as osteolite, and, in combination with calcium chloride and calcium fluoride as apatite. The excrements of carnivorous animals also contain it, and the fossil remains known as coprolites, as well as other extensive mineral deposits, contain a large amount of this phosphate.

Characters.—Tricalcic phosphate is insoluble in water, but is slightly soluble in solutions of sodium chloride, ammonium salts; starch, gelatin, and other organic substances also determine its solution in water to some extent, and it dissolves in larger proportion in water containing carbonic acid. It is readily dissolved by nitric acid or hydrochloric acid, less readily by acetic acid or other organic acids, and it is completely decomposed by sulphuric acid.

The salt is obtained by mixing a solution of calcium chloride with a solution of trisodic phosphate (see p. 276), or by gradually adding a solution of ordinary sodium phosphate mixed with ammonia to solution of calcium chloride; it is a gelatinous precipitate which dries into a white earthy powder. It is not decomposed when heated to redness, but when heated in contact with carbon and silica, carbonic dioxide and phosphorus vapour are given off and calcium silicate is formed.

Uses.—Calcium phosphate, as it occurs in bones, is used in the manufacture of phosphorus (see p. 150) and as manure; the calcium phosphate occurring as apatite, osteolite, coprolites, and in various other forms as minerals, is also largely employed in the preparation of manure, for which purpose it is converted into a more soluble condition by treating the several materials with sulphuric acid so as to form what is technically termed superphosphate, consisting of a mixture of calcium sulphate with acid calcium phosphate, the composition of which approximates to the formula $CaH_4P_2O_8$. Pure tricalcic phosphate treated in this manner should yield a product containing in the dry state acid calcium phosphate equivalent to 61 per cent. of tricalcic phosphate; but since the phosphatic materials employed for the preparation of superphosphate rarely contain more than from 30 to 60 per cent. of tricalcic phosphate, the amount of soluble phosphate in the superphosphate ordinarily met with varies accordingly, and is seldom more than equivalent to 30 or 40 per cent. of tricalcic phosphate.

HYDRAULIC LIME.

The lime obtained by burning certain kinds of limestone possesses the peculiar property when mixed with water of gradually hardening to a stony consistency. This hardening takes place in like manner and to the same extent when lime of this kind has been mixed with water and is entirely immersed under water, on which account hydraulic lime is extensively used for parts of edifices built under water, and it is therefore known as hydraulic lime or water lime. It is also sometimes termed cement, which is, however, an improper designation.

Hydraulic limestones contain as an essential constituent, besides lime, at least 10 per cent. of silica soluble in dilute acids. This silica is either originally contained in the limestones, or is formed during the burning of the limestone from silicates it contains. For preparing hydraulic lime, a limestone is selected that is rich in clay (aluminum silicate). The amount of clay varies considerably. Limestone containing 10 or 20 per cent. of clay yields a poor hydraulic lime, while limestone containing 20 or 30 per cent. of clay affords a good hydraulic lime.

Ordinary hydraulic lime may be considered as consisting essentially of a mixture of burnt lime with soluble aluminum silicate. Since silicates of the kind often occur naturally in the form of trass, pozzolane, santorin earth, etc., hydraulic lime or cement may be prepared by mixing them with the requisite quantity of burnt lime. Cement is the term given to the substance added to burnt lime for the purpose of converting it into hydraulic lime. It is either a material occurring naturally, such as trass, or is artificially prepared, like certain clays which are converted into cements by simple heating.

The hardening of hydraulic lime has been explained in several different ways. Two chief points have, at any rate, been determined which are—(1), the formation of silicates and aluminates, and (2), the formation of hydrates, both of which may be referred to the action of water. When hydraulic lime comes into contact with water, the burnt lime in it first of all forms a hydrate, and some of it dissolves in the water; the lime solution thus formed reacts upon the clay (cement), forming calcium silicate and aluminate. Calcium silicate in its turn combines with water, forming a hydrated silicate.

Besides clay, some other constituents of hydraulic lime also influence its quality. Magnesia when present in certain proportions is beneficial to the hydraulic property of the lime. Limestone containing magnesia, however, requires burning very carefully. Magnesia upon hardening probably gives rise to the production of small quantities of magnesium silicate and aluminate. Ferrous oxide, when present in moderate amount, is also beneficial according to some authorities, but ferric oxide is injurious. Alkalies act beneficially from their property of dissolving silicic acid and alumina, by which means they effect the combination of these substances with lime. A large amount of silicic acid, especially in the state of quartz sand, has an injurious effect, owing to its not being rendered soluble except by a strong heat which produces other injurious changes.

Good hydraulic mortar should not take long in hardening. The first stage of hardening or binding, in the case of good cement under fresh water, ought not to require more than from half an hour to an hour and a half. Cement does not harden so quickly under sea water, requiring from two to three hours. There is also a difference in the heat given off by cement in hardening, some kinds giving off much heat, and others very little. Good cement should not increase in volume during the hardening process. A test for good cement in this respect is that, upon filling a phial with it and immersing the whole for some time under water, the phial should not be burst by the expansion of the cement.

Freshly burnt cement, or hydraulic mortar, hardens more slowly than cement that has been kept for some time in well-closed casks, and it first contracts in volume and then in about fourteen days the volume again increases. It is in the best condition for setting after about two or three weeks.

Preparation.—The methods of preparing hydraulic lime are of three kinds:

1. From natural hydraulic limestone (Roman cement).
2. From burnt lime and natural or artificial cements.
3. From mixture of unburnt lime and clay (Portland cement).

Preparation of Hydraulic Lime from Hydraulic Limestone (Roman Cement).—This kind of cement was at one time exclusively made from a particular kind of argillaceous limestone found in the Island of Sheppy, in the Isle of Wight, and in the London basin. Modern research, has, however, shown that a number of other marls occurring in various parts of the continent are equally well adapted for the preparation of Roman cement. The properties of the burnt lime are chiefly dependent upon the amount of clay in the limestone. If this be known, the quality of the cement

it will yield may be estimated. Looking at the matter from this point of view, Vicat divides the limestone used for preparing cement into different classes, according to the percentage of clay and the quality of hydraulic lime yielded by them.

	Meagre Hydraulic Lime				Hydraulic Lime good quality			Artificial Cements	
	Middling	Ordinary	Very hydraulic	Intermediate	Weak	Ordinary	Excellent	Middling	Ordinary
Calcium carbonate	89	83	80	77	73	64	39	16	2
Clay . . .	11	17	20	23	27	36	61	84	88

Since, however, the composition of the clay itself is of vital importance, in using the above table due consideration must be given to this point.

The limestones used in preparing hydraulic lime vary considerably in composition, as may be seen from the following table. The substances soluble and insoluble in hydrochloric acid are given separately:

	Sheppy stone	Tarnowitz	Hausberger near Minden
Soluble in HCl			
Calcium carbonate .	66·99	49·06	76·82
Magnesium carbonate	1·67	20·32	2·81
Ferrous carbonate .	6·59	16·83	3·21
Alumina . . .	0·39	—	0·89
Insoluble in HCl			
Silica . . .	16·89	3·35	11·03
Alumina . . .	4·32	0·86	2·86
Ferric oxide . .	1·72	0·43	1·86
Lime . . .	traces	0·06	0·12
Magnesia . . .	0·37	0·01	0·05

Burning Roman Cement.—The way in which this operation is carried out is of great influence upon the quality of the cement. Some kinds of stone require longer burning and more gentle heat, others a shorter time but stronger heat. Very siliceous kinds of stone must not be heated very strongly, since this causes the production of large quantities of calcium silicate, and thus the mass may even be partially melted. A mass of the kind whether melted or not is said to be dead burnt, and it is incapable of absorbing water. The stone is therefore only so far burnt as may be necessary to expel the carbonic acid and convert the silica to a state in which it will combine in the wet way with lime. When the burning has been insufficient the cement absorbs water, but does not harden. Limestones, the clay of which contains only a small proportion of bases, are consequently difficult to burn.

When the clay contained in the limestone is plastic and free from sand, a strong but short burning is needed for producing the requisite change in the clay without producing calcium silicate. Should the clay contain admixtures of ferric and manganese oxides or ferric salts, a strong heat is required in order to convert these substances into silicates. The heating may in this case be continued until a slag begins to be formed, and the product thus acquires a grey or brown, and even black, colour. Cement limestones rich in iron, when sufficiently burnt, furnish very good hydraulic lime.

When the limestone contains alkalies, they help to render the silicic acid soluble, by combining with it during the burning. By suitably raising the temperature, fusible double silicates of potassium and sodium, iron, and alumina are formed. These fusible double silicates are essential constituents of good cement. Hydraulic lime prepared from limestone of this kind, when ground, forms a compact powder consisting of minute laminæ, in which the lime particles are protected against the action of the air and moisture by a coating of semi-fused material, for which reason cement of this kind keeps better than ordinary hydraulic lime.

The kilns used in burning hydraulic lime are generally shaft kilns, worked continuously. The pieces of limestone and the fuel are introduced alternately, so that the thickness of the layers of fuel are regulated according to the degree of heat desired.

The composition of hydraulic lime prepared from marly limestone corresponds of course to the sort of marl from which it is prepared. The following table gives the composition of a number of kinds of Roman cement:

	Sheppy	Essex	Bavarian	
Sol. in Hydrochloric acid				
Lime	48·2	46·1	44·96	50·40
Magnesia	2·7	3·7	1·52	1·24
Manganese oxide, Ferric oxide	9·2	12·4	traces 5·83	traces 8·64
Alumina	7·3	4·6	6·43	4·71
Potash	0·8	0·9	0·45	0·50
Soda	0·2	0·1	0·65	0·73
Silica	19·4	17·4	—	—
Carbonic acid	3·4	3·6	4·52	4·61
Phosphoric acid	—	—	—	0·52
Sulphuric acid	—	—	1·20	1·10
Water	1·0	0·7	0·72	1·31
Insol. in Hydrochlor. acid				
Ferric oxide, Manganese oxide, Alumina	1·3	1·7	0·40 — 0·74	traces — 0·70
Quartz	6·2	8·3	32·60	25·29
Silica	0·3	0·5		

Hydraulic Lime prepared by mixing Lime with natural or artificial Cements.—Silicates are found in volcanic regions which contain both silicic acid and alumina in the soluble condition. Such silicates probably originate from hydrated compounds related to clay, which have been changed and dehydrated by volcanic heat. The most important silicates of the kind are trass, puzzolane, and santorin earth.

Trass occurs in several of the valleys branching out from the right bank of the Rhine, where it is quarried and brought into the market either as a powder or in pieces.

The following analyses show the constituents of trass:

	Brohlthal	Holland
Soluble in HCl:		
Lime	3·16	6·5
Magnesia	2·15	1·1
Ferric oxide	11·77	3·9
Alumina	17·70	5·1
Potash	0·29	6 4
Soda	2·44	
Silica	11·50	29·5
Insoluble in Hydrochloric acid:		
Lime	2·25	1·2
Magnesia	0·27	—
Ferric oxide	0·57	—
Alumina	1·25	5·0
Potash	0·08	—
Soda	1·12	—
Silica	37·44	28·0

Puzzolane is a volcanic tufa found in Italy, France, and Belgium. Its composition is as follows:

	Italy	France (Auvergne)
Soluble in HCl :		
Lime	8·0	9·0
Magnesia	0·9	—
Ferric oxide	6·3	21·8
Alumina	9·7	2·0
Potash and Soda	2·6	1·2
Silica	19·5	28·2
Insoluble in HCl :		
Lime	1·2	1·3
Alumina	8·1	6·7
Silica	32·7	25·0
Loss at a red heat	10·2	4·1

Santorin earth is likewise a substance which yields a very good hydraulic lime when mixed with lime. It is found in the island of Santorin, in Algiers, etc.

The following analyses by Feichtinger show the composition of santorin earth used in subaqueous structures in Venice and Fiume:

Soluble in Water.

Calcium sulphate	0·05	Sodium chloride	traces

Soluble in Hydrochloric Acid.

Alumina	1·36	Magnesia	0·23
Ferric oxide	1·44	Silica	traces.
Lime	0·40		

Insoluble in Hydrochloric Acid.

Silica	66·37	Magnesia	1·06
Alumina	12·36	Potash	2·83
Ferric oxide	2·90	Soda	4·22
Lime	2·58	Water	4·06

For preparing hydraulic mortar, these cements are mixed in the powdered state with burnt lime, or lime flour, to which sand is sometimes added, the mortar being prepared in quantities just sufficient for immediate use. The proportion of lime required for a certain cement must be specially ascertained for each kind of cement. For this purpose the cement is mixed in a powdered state with a quantity of lime paste sufficient to form a stiff dough; the mixture is then submerged in water, and must harden within twenty-four hours.

Powdered trass requires—according to the quality of the trass—from 1 to 3 parts of burnt lime. When sand is also employed less trass is taken. Puzzolane requires from half its weight to an equal weight of lime. Additions are often made of sand and other materials, such as pieces of broken pottery, smithy scale, etc. In preparing hydraulic mortar with santorin earth, it is mixed with one third or one fourth of slaked lime and an equal proportion of broken stones.

Among artificial cements added to lime for the purpose of preparing hydraulic lime, the artificial puzzolane manufactured in France is especially worth notice. This is prepared by carefully burning plastic clay containing 2 per cent. of lime. Other cements are made with brickdust, Dutch bricks being especially suitable for the purpose. The slag of blast furnaces, the ash of coal and lignite, etc., also yield hydraulic mortar when mixed with lime.

Regarding the slag of blast furnaces, Huck states that those kinds only are suitable for the preparation of hydraulic lime which gelatinise upon treatment with hydrochloric acid. He further recommends treating the powdered slag before burning with a small quantity of hydrochloric acid, for the purpose of increasing the hydraulic property of the lime.

Hydraulic Lime from unburnt Lime and Clay (Portland Cement).—This kind of cement is prepared in different ways; the raw materials, however, always consist of chalk (or lime) and clay in a finely powdered condition. In order to obtain the chalk in a very finely divided state, it may be with advantage submitted to a process of elutriation. The clay used has a composition which, after burning, approximates

as closely as possible to that of natural cements of good quality, and it is either finely powdered and dried, or sometimes the argillaceous mud of rivers and streams is used.

Pasley's method.—A stiff dough is made by mixing together 10 parts of powdered chalk and one-fortieth of its weight of water, the mixture being then made into balls and kneaded up with 13¾ parts of fresh clay mud from the river Medway. The mass is shaped into bricks and burnt in a continuous shaft furnace. After burning, the bricks are ground up to a fine powder.

Bleibtreu's method.—Chalk that has been elutriated is mixed in the wet plastic condition with clay in the state of fine powder, previously dried, the proportions being 1 vol. clay powder to 2 vols. chalk paste. The whole is intimately kneaded together in a pugmill, and made into bricks, which are dried by placing them upon porous bricks and exposure to the air. The burning of the dry bricks is carried out in a shaft furnace filled with alternate layers of bricks and fuel; this is ignited from below and allowed to burn itself out. When sufficiently cool the bricks are taken out and reduced to powder. Chalk is in some districts replaced by ordinary lime, which is for this purpose allowed to disintegrate and form a fine powder.

The following analyses show the composition of Portland cement:

	From England	From Bavaria
Soluble in HCl:		
Lime	54·10	53·14
Magnesia	0·75	1·59
Manganese oxide	traces	1·30
Ferric oxide	5·30	4·45
Alumina	7·75	3·50
Carbonic acid	2·15	2·10
Phosphoric acid	0·75	—
Soluble in water:		
Sulphuric acid	1·00	—
Potash	1·10	—
Soda	1·66	—
Water	1·00	—
Insoluble in HCl:		
Lime	—	5·59
Ferric oxide	—	3·38
Alumina	—	2·32
Silica	22·23	22·35
Clay, sand	2·20	—

The proportion of water required in the preparation of hydraulic mortar from Portland cement varies with the kind of cement employed, and requires to be determined by trial.

Experience has shown that ordinary hydraulic lime, which retains its firmness and hardness in fresh water, gradually disintegrates when applied to submarine structures. This effect is brought about by the action of the magnesium salts in sea water, and the replacement of the lime in the mortar by magnesia, as may be seen from the following analyses of hydraulic mortar before and after being exposed to the action of sea water.

	I.	II.
Before immersion:		
Lime	13·21	13·92
Silica	57·82	55·65
Alumina	19·73	30·43
Ferric oxide	9·21	—
After immersion:		
Lime	0·25	2·23
Calcium carbonate	3·45	3·38
Magnesia	3·29	7·42
Cement residue	93·00	86·30

No. I. is hydraulic mortar prepared from fat lime and ferruginous artificial cement. No. II. is hydraulic mortar prepared from fat lime and pure clay.

For preparing hydraulic lime to resist the action of sea water, Vicat recommends mixing the finest Roman puzzolane intimately together with 15 per cent. of fat lime. It is essential that the lime should be very fat and that no sand should be mixed with the cement. If trass be used in the place of puzzolane, the mortar decomposes in the course of from five to twelve years. It is also possible to prepare artificial puzzolane which, when mixed with lime, furnishes mortar that resists the action of sea water quite as efficiently as that prepared from Roman puzzolane. For this purpose clay is reduced to a very fine state of division by elutriation, and the moist sediment is formed into balls about 2 in. in diameter, which are dried and burnt in a continuous shaft furnace. The termination of the burning process may be judged of by the reaction of the clay with boiling sulphuric acid. Clay which in the unburnt condition yields 9 per cent. of its mass to sulphuric acid, should, after burning, give up from 16 to 18 per cent.; but when too much burnt very little of it dissolves in sulphuric acid.

Sainte-Claire Deville observed that, when magnesia is immersed in water, a hydrate is formed which, after a time, causes the hardening of the entire mass. This hardening also takes place when the magnesia is mixed with powdered marble, chalk, or ordinary lime. Dolomite calcined at 400° likewise yields, when powdered and made into paste by stirring it with water, a mass which hardens under water. This hardness is due to magnesia and not to lime; for upon heating dolomite sufficiently to expel the carbonic acid of the calcium carbonate, a product is obtained which hardens at once when mixed with water. This property of dolomite has been taken advantage of for industrial purposes.

The following table gives the composition of some varieties of dolomite:

	I.	II.	III.
Magnesium carbonate . . .	61·15	55·23	15·86
Calcium carbonate	21·41	33·99	72·23
Ferrous carbonate (and oxide) . .	8·76	3·85	3·21
Silica	5·58	5·58	2·70
Alumina	2·07	2·27	
Water and organic matter . . .	1·10	3·40	6·00

No. I. yields the Carigeract cement; No. II. the hydraulic mortar of Port Cynfor; No. III. the stucco of Hell's Mouth.

As already mentioned, the product loses its hydraulic property when the dolomite has been so strongly heated that not only the magnesia, but the lime also loses carbonic acid. But if dolomite contain the constituents of cement, silica, alumina, etc., then, upon burning, ordinary hydraulic lime may be formed, besides magnesia, in which case the expulsion of the carbonic acid from the calcium carbonate is advantageous rather than otherwise.

A magnesian cement termed albolith is prepared by burning the magnesite of Frankenstein in Silesia in large retorts something like those used in gas works; the product is ground, sifted, and mixed with amorphous silica. Mixed with magnesium chloride, it yields a very hard plastic mass, applicable as paint.

STRONTIUM.

Symbol Sr. Atomic Weight 87·5.

This elementary substance was discovered in the state of carbonate by Crawford in 1787, as a mineral occurring at Strontian in Argyllshire; its distinct nature was established in 1792 by Hope, and in 1793 by Klaproth. The metal was first isolated by Davy in 1808.

Strontium occurs also naturally in the state of sulphate as cœlestin in small proportion in some kinds of arragonite and brewsterite, as well as in some kinds of mineral water and in sea water.

The metal has a yellow colour like calcium; its specific gravity is 2·542; it oxidises more readily than calcium, and generally resembles the other metals of the alkaline earths; its compounds are also analogous to those of calcium and barium, and they are distinguished by communicating a red colour to the outer portion of the blowpipe flame when heated in the inner portion. Alcohol containing strontium chloride in solution also burns with a red flame.

BARIUM.

Symbol Ba. Atomic Weight 127.

This metal was first recognised in the state of oxide by Scheele in 1774, and it was first isolated in the metallic state by Davy in 1808. It occurs naturally in great abundance in the form of sulphate as heavy spar, and in the form of carbonate as witherite, and with calcium carbonate as baryto-calcite, also in some manganese ores and in mineral water. The physical characters of the metal have not been very accurately determined, but its compounds are closely analogous to those of calcium and strontium.

BARIUM CHLORIDE.

Formula $BaCl_2$. Molecular Weight 198.

Composition.—Crystallised barium chloride contains a molecule of water, its composition being represented by the formula:

$$BaCl_2 + H_2O.$$

Characters.—As usually met with barium chloride forms pellucid crystals belonging to the rhombic system; it is soluble in both cold and hot water, but is very slightly soluble in sulphuric acid, its solubility in the latter menstruum decreasing with the concentration of the sulphuric acid.

When heated, crystallised barium chloride gives off its water of crystallisation, passing over into anhydrous barium chloride, a white pulverulent mass, which melts upon the heat being increased.

Preparation.—The most common sources of barium chloride are witherite, or native barium carbonate, $BaCO_3$, which does not occur in very large quantities, and heavy spar, which is more abundant.

To convert witherite into barium chloride it is dissolved in hydrochloric acid; carbonic acid is evolved, which may be used as a by-product, and barium chloride remains in the solution, which is evaporated to crystallisation.

Barium chloride is also obtained as a by-product in soda works by conducting the hydrochloric acid escaping from the sulphate furnaces through carboys containing witherite suspended in water (*vide* p. 253).

The preparation of barium chloride from heavy spar, $BaSO_4$, is more difficult than its preparation from witherite.

At the time when the consumption of barium chloride was inconsiderable this substance was prepared by heating to redness a mixture of powdered heavy spar and charcoal, so as to reduce it to barium sulphide in the manner represented by the following equation:

$$BaSO_4 + 4C = BaS + 4CO.$$

By lixiviating the fused mass with water, the barium sulphide is dissolved out, and it is converted, by addition of hydrochloric acid, into barium chloride, while sulphuretted hydrogen is evolved. The large quantity of sulphuretted hydrogen thus produced renders this method generally inapplicable.

In order to secure intimate contact between the powdered charcoal and heavy spar, these substances are mixed together with linseed meal and water into a paste, which is kneaded up and moulded into cylinders 3 inches long and 1 inch thick. These cylinders are piled up in layers alternating with layers of coal, in a furnace, and heated to bright redness, care being taken to avoid access of air. Heating in closed crucibles causes too great a consumption of fuel. After lixiviation and decomposing the liquor with raw hydrochloric acid, a good deal of iron remains in solution; the liquid is therefore treated with just sufficient barium sulphide to produce a weak alka-

line reaction. By this means iron is precipitated as sulphide; the precipitate is then allowed to deposit, and the clear liquid drawn off and evaporated to the point of crystallisation.

The method adopted by Kuhlmann for decomposing barium sulphate is easier. An intimate mixture of coal and heavy spar is placed in the hinder part of a double reverberatory furnace, and mixed with a quantity of solution of manganous chloride (by-product in the preparation of chlorine, the free acid of which has been neutralised by lime, *vide* p. 165), and well stirred meanwhile, until, after evaporation of the water, a stiff doughy mass is obtained. The mass thus formed is then brought into the anterior part of the furnace nearest the fire, where it is heated for an hour to redness. The semi-liquid mass is then drawn out, allowed to weather in the air for a few days, lixiviated, and the liquor crystallised. Should the liquor contain an excess of barium sulphide it is decomposed by manganous chloride, and any excess of manganous chloride is neutralised with barium sulphide.

The essential features of this method are the same as in the first-mentioned process: the barium sulphate is reduced by carbon to barium sulphide, which, together with manganous chloride, yields manganese sulphide and barium chloride. The presence of ferric chloride is a matter of indifference in this process, since it behaves in a manner exactly analogous to manganous chloride.

The process of reduction is quicker by this method because the mass melts, and thus a more intimate contact of the ingredients is effected. This method has also the advantage that the heating may be carried out in a reverberatory furnace.

Godin's method consists in heating together in a reverberatory furnace charcoal, heavy spar, calcium chloride and limestone, lixiviating the mass with water, and evaporating to crystallisation. The calcium sulphide thus formed, being insoluble, remains undissolved.

The method of Asselin and Wagner consists in heating to redness a mixture of heavy spar, charcoal, and tachydrite ($CaCl_2 + 2MgCl_2$).

Uses.—The consumption of barium chloride has increased considerably of late, in consequence of its use for softening water used in steam boilers. As already shown, water containing gypsum is not suitable for boilers, owing to its forming a very hard crust, and where only water of this kind is available for use, it is first of all treated in large basins with barium chloride. The process which takes place consists in the conversion of the gypsum and barium chloride into calcium chloride and barium sulphate, which settles to the bottom of the basins in the form of a fine sand, while the calcium chloride remains in solution, but forms no hard crust or scale when the water is used in the boiler. The addition of barium chloride to water containing gypsum is equally effective if the salt be added before the water enters the boiler, and without waiting for the barium sulphate to deposit.

Besides this application of barium chloride, the substance is used in the preparation of baryta white (barium sulphate) and other preparations of the metal. Barium chloride is used in dyeing with Saxon blue, owing to its forming a very fast colour with indigo dissolved in sulphuric acid.

BARIUM SULPHATE.

Formula $BaSO_4$. Molecular Weight 223.

Occurrence.—Barium sulphate occurs naturally as heavy spar, in considerable quantities.

Characters.—Artificial barium sulphate, or baryta white, is a very finely divided pulverulent substance of dazzling whiteness and great covering power. When carefully prepared it resists all atmospheric influences. Baryta white has the advantage over white lead of not being blackened by sulphuretted hydrogen; it covers better also than zinc white, and is cheaper than either. Baryta white cannot, however, be used with oil, on account of its mixing but imperfectly with that medium and consequently covering badly.

It is generally used stirred up with about 30 per cent. of water to a paste.

Preparation.—Baryta white is prepared either directly or is obtained as a by-product.

It is prepared by mixing an aqueous solution of barium chloride in the cold with sulphuric acid of sp. gr. 1·262 as long as a precipitate is produced, allowing the precipitate to settle, and washing it with water until the wash water ceases to show an acid reaction. The washed barium sulphate is then placed on a linen cloth to drain, and is ready for the market.

If the barium sulphate were to be thoroughly dried it would lose in covering power; the same evil would be caused by precipitating the sulphate from a hot solution, owing to the formation of a coarse crystalline powder; when it is precipitated cold, an impalpable amorphous powder is produced.

In preparing baryta white from barium chloride, the liquor resulting from the preparation of barium chloride may be used, which must, however, be free from sulphide, otherwise sulphur would be precipitated along with the sulphate, and render it impure. The presence of free sulphur in baryta white, and the formation of sulphuric acid—owing to oxidation of sulphur in the air—would cause the destruction of other colours mixed with it.

In order to obtain a barium chloride liquor pure enough for preparing baryta white, the barium sulphide liquor (page 298) is decomposed with a slight excess of hydrochloric acid, and boiled by passing steam into it until no further smell of sulphuretted hydrogen is noticeable.

In preparing baryta white from witherite, the mineral is either first completely converted into barium chloride (according to Hahn a 10 per cent. solution is the best), and this is treated with sulphuric acid, or according to Pelouze's method—which is better—the two reactions are conducted simultaneously by treating finely powdered witherite with dilute sulphuric acid containing from 2 to 4 per cent. of hydrochloric acid. The process consists in the conversion of the barium carbonate into barium chloride by the hydrochloric acid, and in the conversion of the barium chloride into sulphate by the sulphuric acid, while the hydrochloric acid is again liberated; so that a small quantity of hydrochloric acid is in time capable of dissolving a large quantity of barium carbonate. When witherite contains galena, as is often the case, the method is not applicable on account of the galena not being decomposed, and colouring the product.

Baryta white is obtained as a by-product in a number of industrial operations. In nearly every instance where calcium carbonate is used for neutralising sulphuric acid, barium carbonate can be used in its place, so as to obtain barium sulphate instead of calcium sulphate, as a by-product. Instances of the kind are the manufacture of caustic soda and potash, tartaric acid, starch, sugar, etc.

Wagner suggests the use of baryta instead of lime for the saponification of fats in the manufacture of stearic acid, by which means barium sulphate would be obtained instead of gypsum.

Uses.—As already mentioned, baryta white is not well adapted for use as an oil colour, since the mixture has a very imperfect covering power as paint. A paint of good covering power is, however, obtained by mixing together equal parts of baryta white and zinc white. Large quantities of baryta white are employed in the preparation of wall papers, coloured papers, playing cards, etc. It seems to be especially useful in preparing papers to which it is desired to give a satin lustre. Baryta white is especially adapted for mixing with other colours on account of its neutral characters and the difficulty with which it is decomposed. It forms also a useful addition to paper pulp; paper thus prepared has a dazzling white appearance, and is almost opaque.

Powdered heavy spar is chiefly employed as a diluent or an adulterant for other white colours (white lead, zinc white, etc.) and as an admixture with colours like ultramarine, chrome yellow, etc. It is used unmixed as a cheap paint, but on a comparatively small scale. It is also employed, but at present not to any great extent, in the manufacture of glass.

Although heavy spar is chemically the same as the artificially prepared barium sulphate called blanc fix, it cannot like the latter be used as a paint, on account of its great density.

ALUMINUM.

Symbol Al. Atomic Weight 27·5.

History.—It is probable that Oersted first obtained aluminum in the metallic state, for in 1824 he decomposed moist aluminum chloride with sodium amalgam. However the first definite account of aluminum was given in 1827 by Wöhler, who obtained it by heating aluminum chloride with potassium. Bunsen first used the double aluminum and sodium chloride for preparing aluminum by decomposing it electrolytically. The native aluminum and sodium fluoride known as cryolite was first used in the preparation of aluminum by H. Rose. But the successful preparation of aluminum industrially is chiefly due to the efforts of H. Sainte-Claire Deville; for though he did not introduce any essentially new method of preparation, and the means of carrying out his experiments were furnished by the French Academy, his modifications of the old methods served to make them practicable for industrial purposes. The use of sodium in the preparation of aluminum in the place of potassium is due to him.

Occurrence.—Aluminum does not occur naturally in the free state, but in combination with oxygen it is one of the most abundant and widely distributed elements. The oxide or alumina, however, is itself of comparatively rare occurrence in the different forms of corundum, known as the ruby, sapphire, and emery; and it occurs for the most part in the form of saline compounds, especially silicates, as andalusite, cyanite, sillimanite, clay, etc., in which state, and combined with other silicates, aluminum exists in felspar, mica, hornblende, etc. In the form of sulphate it occurs as alunite or alumstone; wavellite is an aluminum phosphate, and aluminum fluoride is an essential constituent of cryolite and topaz. Aluminum hydrates occur as gibbsite and diaspore.

Characters.—Aluminum in a compact state is a greyish white metal of considerable lustre, and it gives a clear ringing sound when struck. Its specific gravity is 2·5, and it admits of being beaten out into sheet, as well as of being drawn into wire; its tenacity is between zinc and tin; it is not very flexible; and it melts at 700°. The industrial value of aluminum is chiefly due to its resistance to the influence of oxidising agents; at the ordinary temperature of the air it is entirely unaltered, and it may even be heated to redness without being much oxidised. Aluminum does not decompose water even at a red heat, neither is the metal acted upon by sulphuretted hydrogen, owing to the slight affinity between aluminum and sulphur. Upon melting together a mixture of aluminum and silver sulphide, sulphur is liberated, and an alloy of aluminum and silver is formed. Aluminum is very little acted upon by dilute sulphuric acid, but it is very energetically attacked by dilute hydrochloric acid, forming aluminum chloride and free hydrogen. Aluminum is not attacked by dilute or concentrated nitric acid, and boiling sulphuric acid acts very slowly on the metal. Caustic potash and soda dissolve aluminum, forming soluble aluminates, with evolution of hydrogen. Ammonia exerts very little action upon the metal.

Commercial aluminum is always contaminated with silicon and iron. Rammelsberg found in a sample between 2 and 10 per cent. of silicon, and the amount of iron is sometimes as much as 6 per cent. and upwards.

Preparation.—Wöhler's method of obtaining this metal consists in decomposing aluminum chloride with potassium; but at the present day it is prepared either from the double aluminum and sodium chloride prepared artificially, or from natural cryolite (aluminum and sodium fluoride).

From Aluminum and Sodium Chloride.—The essential feature of this process consists in mixing the aluminum and sodium chloride with sodium, common salt, and fluor spar, and exposing the mixture to a temperature sufficient to cause the sodium to abstract the chlorine from the aluminum chloride, and liberate aluminum. The common salt serves as a flux, and the addition of fluor spar serves to dissolve small quantities

of alumina produced by the action of moisture upon the aluminum chloride and it is essential, not only because alumina is not reduced by sodium, but also because the alumina formed covers the granules of aluminum produced and prevents their fusing together to a homogeneous mass.

For preparing aluminum, Sainte-Claire Deville, Morin, and Debray recommend the following mixture:—

Aluminum and sodium chloride	400 parts
Sodium	75·80 „
Common salt	200 „
Fluor spar	200 „

The aluminum and sodium chloride is mixed with the salt and fluor spar, both thoroughly dried, and finely powdered; alternate layers of this mixture of sodium are then placed in a crucible covered with a layer of common salt and gradually heated in a reverberatory furnace until the crucible and its contents acquire a white heat, the melted mass being continually stirred during the operation. Upon pouring the contents of the crucible upon a cold stone floor, the greater part of the aluminum is obtained as a compact lump; the small granules which remain dispersed through the slag are afterwards, as far as may be, collected separately.

Morin heats the mixture in a reverberatory furnace, instead of crucibles, the hearth being constructed so that the aluminum collects in a hollow and there melts to a compact mass. He recommends a mixture consisting of:

Aluminum and sodium chloride	100 parts
Sodium	20 „
Fluor spar	50 „

Cryolite may always be used with advantage in place of fluor spar. It acts both as a solvent for alumina like fluor spar, and also increases the yield by furnishing some aluminum. When cryolite is substituted for fluor spar, the following mixture may be used:—

Aluminum and sodium chloride	110 parts
Sodium	35 „
Cryolite	40 „

From Cryolite.—When cryolite and sodium are melted together in the presence of a flux, the fluorine of the cryolite combines with the sodium, and aluminum is liberated in the metallic state. The mixture used in the Rouen aluminum manufactory consists of:

	H. Rose.	Wöhler.
Cryolite	50 parts	16 parts
Sodium	20 „	12½–15½ „
Potassium chloride	50 „	9 „
Sodium „	—	7 „

The mixture of finely-powdered cryolite and potassium chloride or sodium chloride is placed in alternate layers with slices of sodium in a crucible, which is then strongly heated in a reverberatory furnace. When the reaction is complete, the melted mass is poured into iron moulds, the aluminum detached from the slag, remelted and cast into ingots.

Dumas gives the following as the results of analyses of commercial aluminum:—

Aluminum	92·5	96·16
Silicon	0·7	0·47
Iron	6·3	3·37

Uses.—The chief use of aluminum is in the manufacture of fancy articles; for instance, jewellery for setting stones, bracelets, watch cases, brooches, seals, penholders, studs, handles of knives and forks, spectacles, opera glasses, etc., etc., for which purposes it is especially fitted, owing to its not being attacked by sulphuretted hydrogen. Aluminum is very useful for articles in which comparative strength combined with great lightness is required, such as tubes for optical instruments, small weights, surgical instruments, etc., etc. Pens made of aluminum are more durable and lighter than those made of steel.

Aluminum is not well suited for coinage, owing to its fluctuating value, and further because it loses its value when dissolved; it may be used in making medals, counters, etc.

Compounds.—Aluminum forms only one series of compounds, and as compared with hydrogen or chlorine it is trivalent; but since these compounds appear to contain two atomic proportions of aluminum united in the molecules, it is probably

tetravalent and only apparently trivalent. The compounds of aluminum present close analogies with some of those of iron and chromium; the composition of the chloride is represented by the formula Al_2Cl_3, that of the oxide by the formula Al_2O_3, and the sulphate is Al_23SO_4. Most aluminum compounds combine with corresponding compounds of monovalent elements, forming double salts; thus the chloride combines with sodium chloride, the sulphate with potassium sulphate, and the oxide with water forming double salts, as shown by the following equations:

$Al_2Cl_4 + 2NaCl = 2AlNaCl_4$ sodic aluminum chloride.
$Al_23SO_4 + K_2SO_4 = 2(AlK2SO_4)$ potassic aluminum sulphate.
$Al_2O_3 + H_2O = 2AlHO_2$ monohydrate.

Besides the hydrate represented by the last formula, there are two others, a trihydrate AlH_3O_3, and an intermediate dihydrate $Al_2H_4O_5$, with other basic oxides. The oxide also forms compounds of a similar nature, which are termed aluminates; thus, for instance, a potassic compound analogous to the monohydrate has a composition represented by the formula $AlKO_2$, and several compounds of the same kind occur naturally; for instance, the zinc aluminate Al_2ZnO_4, as gahnite, and magnesium aluminate Al_2MgO_4, as spinel. The sodium compound $AlNa_3O_3$ is used as mordant in calico-printing, and is produced artificially for that purpose.

The oxygenated compounds of aluminum and silicon are among the most important of the natural substances containing aluminum. All the different kinds of clay consist essentially of an aluminum silicate, but the relative proportions of their constituents vary considerably. Aluminum silicates combine with other silicates to form double salts, and a very large proportion of the minerals which constitute the various crystalline rocks are substances of this nature.

The compounds of aluminum are generally colourless. Those which are soluble in water have a sweetish astringent taste. Many of the saline compounds are quite insoluble in water, but they are readily dissolved by hydrochloric acid or sulphuric acid, unless they have been strongly heated.

The alloys of aluminum are of great interest and importance; with tin it forms a very hard alloy; with copper the well-known gold-coloured alloy known as aluminum bronze.

This alloy of aluminum and copper is much used for making artificial jewellery, etc. It possesses great lustre, hardness, and durability; the proportions are generally 10 per cent. of aluminum and 90 per cent. copper. The hardness of this alloy in the cast state is between iron and steel; when hammered its hardness approaches that of steel.

Owing to the great hardness of aluminum bronze, it might be used with advantage for plumber blocks if sufficiently cheap. Experiments made with this object gave excellent results.

An alloy of 96 per cent. aluminum and 4 per cent. silver has a white colour and considerable lustre. It would answer well for table plate.

ALUMINUM CHLORIDE.

Formula Al_2Cl_6. Molecular Weight 268.

This salt is a yellowish crystalline substance volatilisable at a moderate red heat. It is deliquescent and very soluble in water; when the solution is evaporated to dryness, decomposition takes place and alumina is formed, together with hydrochloric acid, which escapes.

Preparation.—For preparing aluminum chloride on the small scale, either a tubulated glass retort, coated with fire clay, or a porcelain retort, is filled with an intimate mixture of alumina and charcoal made into a paste with oil; the retort is then placed in a reverberatory furnace, with the neck protruding, and heated to redness, while at the same time chlorine is passed into the retort. Aluminum chloride distils over, condensing in the neck of the retort and receiver as a mass of laminar crystals.

For preparing this salt on a large scale Sainte-Claire Deville recommends the use of a fire-clay gas retort set upright, at the bottom of which is an opening that can be closed by a close-fitting slide, while the upper end is fitted with a lateral delivery tube, through which the vapour produced in the retort passes into a condensing chamber. In working the apparatus the retort is filled with a mixture of alumina, coal tar, and charcoal, heated to redness, and dry chlorine, passed into the retort at the lower part of it, the mouth being closed directly vapour of aluminum chloride begins to appear in large quantity. The heating and supply of chlorine are continued as

long as aluminum chloride is formed, and then the slide at the bottom of the retort is opened, the residue drawn out, and the retort charged again.

ALUMINUM OXIDE (ALUMINA).

FORMULA Al_2O_3. MOLECULAR WEIGHT 103.

History.—This substance was first shown to be distinct from lime in 1754 by Marggraff, who pointed out that the earth obtainable from alum does not disengage ammonia from sal ammoniac, and that its saline compounds are quite different from those of lime; he also showed that clay contained this earth in combination with silica. Some years before this, however, Hellot had described the earth obtained from clay by means of sulphuric acid and subsequent precipitation by fixed alkali, as being almost insoluble in acids after it had been heated to redness. The solubility of moist alumina in caustic alkalies was first observed by Klaproth in 1789.

Occurrence.—Alumina occurs naturally as corundum or adamantine spar, the purer crystalline varieties of this mineral constituting the ruby and sapphire: the impurer variety, termed emery, contains a considerable amount of ferric oxide.

Characters.—Crystallised alumina is next to the diamond the hardest substance known; its density is about 3·9; the purer natural varieties are transparent or translucent, and in the pure state it is colourless; the colour varies from white or grey to blue, red, yellow, and brown, owing to the presence of minute proportions of metallic oxides; the more impure varieties are opaque and dark-coloured. In the crystalline condition alumina is quite infusible and insoluble in acids. This is also the case with artificially prepared alumina, especially after it has been heated to redness; but by fusion with acid sulphate of potassium or with alkaline hydrates it is rendered soluble.

Alumina combines with water in three proportions, forming hydrates; the monohydrate $AlHO_2$ occurs naturally as diaspore.

The trihydrate AlH_3O_3 also occurs naturally as gibbsite; it is obtained as a gelatinous precipitate by adding an alkali to the solution of an aluminum salt, and when dried at a moderate heat it is a soft friable mass, soluble in acids and caustic alkalies; it adheres to the tongue, and forms a stiff paste with water, but is insoluble in that liquid. At a red heat it gives up its water and contracts considerably. This hydrate has a marked capacity of combining with some neutral organic substances, and the pigments termed lakes are of this nature. The fibres of cotton impregnated with alumina acquire the power of retaining colour substances, and on this account aluminous salts are used as mordants for producing fast colours in dyeing and calico-printing.

The dihydrate $Al_2H_4O_5$ is formed when a dilute solution of aluminum diacetate is exposed for several days to a temperature of 100° in a close vessel; the salt appears to be decomposed, and acetic acid liberated, though the alumina is not precipitated and it remains dissolved when the solution is boiled in an open vessel to drive off the acetic acid. The solution is coagulated on the addition of mineral or vegetable acids, and by decoctions of dye woods, but the alumina it contains does not act as a mordant. On evaporation to dryness, the dihydrate remains in a condition insoluble in strong acids, but soluble in acetic acid. By boiling with solution of potash it is converted into the trihydrate.

Preparation.—Alumina may be prepared by igniting aluminum sulphate or ammonia alum, or by adding ammonium carbonate to a boiling solution of an aluminum salt, washing the precipitate, and drying it at a moderate heat or by ignition, accordingly as the alumina is required to be in the state of hydrate or anhydrous.

ALUMINUM AND SODIUM CHLORIDE.

FORMULA $AlNaCl_4$. MOLECULAR WEIGHT 192·5.

Preparation.—This double salt may be prepared by heating up to 200° for a short time a mixture of equal molecular proportions of aluminum chloride and sodium chloride; the combination takes place with considerable development of heat. To obtain aluminum and sodium chloride directly, a retort coated with fire clay is filled with a mixture of alumina, coal tar, charcoal, and common salt, heated to redness, and chlorine passed into it. The aluminum chloride thus formed, combines with the sodium chloride, forming the double salt which distils over; but as it is less

volatile than aluminum chloride, a higher temperature is required. However, by this direct method, an operation is saved, and it is generally adopted.

The alumina used in the preparation of aluminum chloride (or the double salt) is obtained in different ways. Sainte-Claire Deville recommends the use of calcined ammonia alum. Impure cryolite also yields a useful alumina, when boiled in fine powder with milk of lime, by which it is converted into soluble sodium aluminate and calcium fluoride, which remains undissolved. The clear solution is decanted off and carbonic acid passed through it, by which means sodium carbonate is formed and remains in solution, while aluminum hydrate is precipitated; this is separated from the solution and dried, the soda solution being evaporated to obtain soda for preparing metallic sodium.

Other porous kinds of alumina may be used in the preparation of aluminum, but care must be taken that they are free from iron, otherwise the aluminum prepared from them is apt to be contaminated with that metal.

ALUMINUM SULPHATE.

Formula $Al_2 3SO_4 + 18H_2O$. Molecular Weight 667.

This salt occurs in commerce under the name of alum cake, or concentrated alum, and is now often used in the place of ordinary alum.

Characters.—Aluminum sulphate dissolves in two parts of water, and upon evaporating the salt crystallises in pearly scales, which form a crystalline mass when separated from the mother liquor and dried. The salt melts in its water of crystallisation upon cooling. The amounts of salt in solutions of different density are indicated in the following table:

Degrees Baumé	Specific gravity	Aluminum sulphate	Degrees Baumé	Specific gravity	Aluminum sulphate
1	1·007	8·64	17	1·123	156·7
2	1·013	17·29	18	1·132	166·5
3	1·020	25·95	19	1·140	176·4
4	1·027	33·72	20	1·148	189·2
5	1·033	41·51	21	1·157	202·1
6	1·040	49·29	22	1·166	215·0
7	1·047	57·08	23	1·174	227·9
8	1·055	67·20	24	1·183	241·9
9	1·062	77·50	25	1·192	255·9
10	1·069	86·9	26	1·201	269·9
11	1·077	97·2	27	1·211	283·9
12	1·084	107·4	28	1·220	297·6
13	1·092	117·3	29	1·230	311·3
14	1·099	127·1	30	1·239	325·0
15	1·107	137·0	31	1·249	338·9
16	1·115	146·8	32	1·260	352·8

The following table gives the results of analyses of different kinds of aluminum sulphate:

Locality	Plympton	Schwermsal	—		
Analyst	Muspratt	Wegand	H. Fleck		
Aluminum sulphate	51·00	53·70	47·35	50·80	51·63
Sodium sulphate	—	—	4·35	1·24	0·77
Free sulphuric acid	—	—	0·73	0·27	—
Ferric oxide	—	1·15	—	—	—
Potash	—	0·62	—	—	—
Water	49·00	45·79	47·37	47·47	46·94

Preparation.—Aluminum sulphate is prepared from various raw materials, such as clay, cryolite, bauxite, etc.

From Clay and Sulphuric Acid.—For preparing aluminum sulphate from clay, the purest kind of clay is selected, kaolin, or pipe clay, being the most suitable kind, care being taken that the clay contains only traces of lime and iron. The clay is first heated to redness in a reverberatory furnace, and thus loses its plastic consistency, becoming porous and friable, while any ferrous oxide is converted into ferric oxide, which is less easily attacked by sulphuric acid when it has been heated to redness.

The calcined clay is reduced to a fine powder and sifted to separate coarse pieces, then heated with sulphuric acid of sp. gr. 1·462 to 1·490. The treatment with acid may be carried out either by mixing the clay in a pan covered with a brick arch with about two-fifths of its weight of sulphuric acid, and heating the whole to about 70° by making the flame of a reverberatory furnace pass under the arch, or a wooden trough lined with lead may be used for mixing the clay and sulphuric acid, allowing the mass to remain 24 hours at the ordinary temperature, and then slightly heating it in leaden pans for a few hours. The action of sulphuric acid upon clay consists in decomposing the aluminum silicate, with formation of aluminum sulphate and free silicic acid. The process is considered complete when no free sulphuric acid remains in the mixture, which may be ascertained by testing a filtered portion of the liquid with a solution of sodium hyposulphite, when no precipitate or cloudiness should be produced. Another test consists in plunging a strip of zinc into the liquid; no escape of hydrogen indicates the absence of free sulphuric acid.

The clay, after treatment with sulphuric acid, is placed in wooden lixiviating vessels lined with lead, and stirred up with water to a thin paste. After a time the silica and undissolved clay settle to the bottom, leaving a clear solution above. The first and strongest solution, having a specific gravity of 1·109 to 1·134, is evaporated in leaden pans by the waste heat of the calcining furnaces, and the weaker solutions are used for lixiviating fresh quantities of crude sulphate.

The solution, after being evaporated to a specific gravity of about 1·152, is allowed to settle in tanks, and the clear liquid evaporated till it has a specific gravity of 1·357 or 1·420, and forms when cold a hard mass; it is then run into moulds made of lead. When the solution contains iron, a small quantity of yellow potassium prussiate is added to it while in the settling tanks, which forms an insoluble precipitate of Berlin blue, that settles out with the other insoluble impurities at the bottom.

From Cryolite.—The preparation of aluminum sulphate from cryolite ($AlF_3 + 3NaF$) is always carried out in connection with the manufacture of soda or sodium hydrate. (See p. 270.)

From Bauxite.—This mineral, containing from 60 to 75 per cent. of alumina, is mixed with calcined sodium carbonate and heated in a reverberatory furnace. The mass then lixiviated yields a solution of sodium aluminate, which is decomposed by carbonic acid and the alumina precipitated; after washing the alumina, it is heated with sulphuric acid in the usual way.

Bauxite may also be decomposed either by heating it to redness with sodium sulphate and charcoal, or by boiling it with caustic soda. In both cases sodium aluminate is formed, which is treated in the manner above described. Sodium aluminate is also formed by passing superheated steam over a mixture of bauxite and common salt.

The methods above described involve the consumption of a large quantity of fuel for dissolving the aluminum hydrate in sulphuric acid; and insoluble basic aluminum sulphate is liable to be formed. Pemberton has, therefore, introduced the following method by which these inconveniences are got rid of. A quantity of moist aluminum hydrate (containing 38 per cent. of aluminum hydrate) is mixed with such a quantity of sulphuric acid that the whole corresponds to the composition of the aluminum sulphate, inclusive of the 18 molecules of water. The rise of temperature caused by the mixing is sufficient when large quantities are operated upon to determine the solution of the alumina in the sulphuric acid, and upon cooling the whole forms a hard mass. When bauxite is used for preparing aluminum sulphate, soda and caustic soda are always produced at the same time. (See p. 271.)

From Blast Furnace Slag.—Lürmann's process consists in heating the granulated slag with hydrochloric acid in a vat covered with a lid, to dissolve the alumina, which is then precipitated by adding finely powdered calcium carbonate. The precipitate, after being washed, is dissolved with sulphuric acid, the clear liquid drawn off from the undissolved silica, and evaporated. Owing to the fact that ferrous oxide is not precipitated by calcium carbonate, aluminum sulphate thus prepared is but little contaminated with iron, provided the access of air is prevented, after adding the calcium carbonate.

Uses.—Aluminum sulphate may be used in nearly all cases as a substitute for alum and since the useful qualities of alum are essentially due to the alumina contained in that salt, it is obvious that there is an advantage in using aluminum sulphate, instead of ordinary alum, inasmuch as it is cheaper, and contains a larger amount of alumina; it is also more soluble than potash alum. Aluminum sulphate has, however, some disadvantages; it is apt to contain an excess of acid and varying amounts of water; so that before using a sample of the salt it is necessary to ascertain the amount of water it contains; it is also more difficult to obtain aluminum sulphate as free from iron as ordinary alum.

POTASSIUM AND ALUMINUM SULPHATE (ALUM).

Formula $AlK,2SO_4 + 12H_2O$. Molecular Weight 474·6.

History.—The history of this salt is rendered somewhat uncertain, not only by the fact that in early times it had different names, but also because the term alum (*στυπτερία* of the Greeks and *alumen* of the Romans) was applied to very different substances.

The substance termed *στυπτερία* was known before the fifth century. It was mentioned by Herodotus in the first century of the Christian era, and Dioscorides described it as being found in Egypt, upon Melos, in the Lipari Islands, in Sardinia, Macedonia, Phrygia, Armenia, etc. Pliny, who is the first author that makes mention of *alumen*, speaks of several kinds: white alum, used for dyeing wool bright colours, and black alum, for giving a dark colour. The same author mentions that alum is coloured black by galls.

Hence it follows that the ancients either had no true alum, or at least it must have been considerably contaminated with iron, for pure alum is not coloured by gall nuts. Most probably the *στυπτερία* of the Greeks and the *alumen* of the Romans was a mixture containing alum and a large quantity of iron sulphate.

The Arabian chemist Geber, who lived in the eighth century, was certainly acquainted with pure alum. In his day, large quantities of alum came into the market from the East. The same chemist described the burning of alum.

At the time of the taking of Constantinople by the Arabians, the manufacture of alum was introduced into Italy by De Castro, who learnt the method of preparing it during his travels in the East; and on returning to his native country, recognised, near Tolfa, a plant which he had observed to be characteristic of the alum districts in the East. Upon examining the soil it was found to contain alum, and the immediate result was the foundation (in 1458) of alum-boiling works on the spot. Soon afterwards the manufacture of alum was commenced in Germany. The alum works near Dübein existed at the beginning of the sixteenth century.

The alum works of Liége were famous at the beginning of the present century. In 1806 there were no less than 23 alum works in the neighbourhood, and even at an earlier period South Germany was entirely supplied with alum from Liége.

Occurrence.—Alum occurs naturally, but only in small quantities, chiefly in volcanic districts, as an efflorescence on the surface of fissures in lava; also in coal districts, as at Saarbrücken, and upon alum shale.

The mineral known as alunite occurs in much larger quantities than alum itself in volcanic districts, and its composition is similar to that of alum, being represented by the formula:

$$Al_2 3SO_4 + K_2SO_4 + 2Al_2O_3,12H_2O.$$

Composition.—Potash alum is a double salt containing aluminum sulphate and potassium in the state of sulphate, combined with water of crystallisation.

Characters.—Alum is a colourless transparent substance, crystallising in forms belonging to the regular system, generally in octahedra. When heated to 60°, alum loses 18 molecules of water. At a still higher temperature it gives off the remainder of its water of crystallisation, swells up considerably, and is converted into burnt alum. It is soluble in water, more so in hot than in cold water.

The following table gives the proportion of alum dissolved by 100 parts of water at different temperatures:—

Temp. C.	Amount of Alum dissolved	Temp. C.	Amount of Alum dissolved
0°	3·90	60°	66·65
10°	9·52	70°	90·67
20°	15·13	80°	134·47
30°	22·01	90°	209·31
40°	30·92	100°	357·48
50°	44·11		

Upon adding ammonia in excess to an aqueous solution of alum, pure aluminum hydrate is precipitated; but basic aluminum sulphate is precipitated when the ammonia added is not quite sufficient to decompose all the alum in solution. By carefully adding to a solution of alum sodium carbonate, but not sufficient to cause a permanent precipitate, a solution of basic aluminum sulphate is obtained, known as neutral alum. By heating this solution, basic aluminum sulphate is precipitated, and when the solution is allowed to evaporate slowly in the air, cubic crystals of alum are obtained. This cubic alum occurs in Roman alum. A solution of neutral alum may also be prepared by treating a solution of alum with freshly precipitated aluminum hydrate, until it ceases to be dissolved.

Roman Alum differs from ordinary alum in containing rather more alumina, and in being crystallised in cubes, instead of octahedra. It dissolves in water without change, but upon heating the solution to 42° basic alum is deposited; and the solution contains ordinary alum, which crystallises in octahedra. Roman alum is characterised by great purity, but it generally presents a slightly rubbed appearance, and is often covered with a reddish earth.

The term alum is now applied to a number of salts having a composition analogous to that of potash alum, but having either the aluminum or the potassium replaced by kindred metals. The following formulæ represent the relations of some of these salts:—

Potash alum	$Al_2 3SO_4 + K_2\ SO_4 + 24H_2O$	=	$2(AlK\ 2SO_4 + 12H_2O)$
Chrome alum	$Cr_2 3SO_4 + K_2\ SO_4 + 24H_2O$	=	$2(CrK\ 2SO_4 + 12H_2O)$
Soda alum	$Al_2 3SO_4 + Na_2\ SO_4 + 24H_2O$	=	$2(AlNa\ 2SO_4 + 12H_2O)$
Ammonia alum	$Al_2 3SO_4 + 2NH_4SO_4 + 24H_2O$	=	$2(AlNH_4\ 2SO_4 + 12H_2O)$

Since potassium salts are comparatively dear, and the action of alum is essentially due to the alumina it contains, potash or ordinary alum has of late been considerably replaced by ammonia alum.

Preparation.—Alum is prepared from various raw materials. Small quantities are extracted from certain kinds of lava, and Roman alum is prepared from alum stone; but the greater part of the alum of commerce is prepared from alum shale.

Preparation from Lava.—The alum found in volcanic districts is no doubt formed by the action of free sulphuric acid, originating by the oxidation of sulphur and sulphuretted hydrogen in moist air, upon lava containing alumina and potash. Alum is also formed by the action of volcanic heat upon alum stone, in the Auvergne, in solfatara, and in burning coal seams; in each instance it occurs mostly as an efflorescence.

In solfatara the efflorescence of alum is promoted by increasing the surface exposed to the air by breaking the lava into small pieces and stacking them up in walls; the alum is then extracted by lixiviation, and the solution evaporated by the natural heat of the soil (about 40°). This source of alum is however very unimportant.

Alum from Alum Stone.—This mineral, known as alunite, occurs imbedded in volcanic rocks, but only in small quantities. The most important source of alum stone is at Tolfa, near Civita Vecchia, where there are large alum works. Alum stone also occurs in the Duchy of Piombino, near Montioni in Tuscany, near Tokay in Hungary, on Mont Dore in France, and in some of the islands in the Grecian Archipelago (Milo, Nipoligonte). Alum stone also occurs at Zabreze, in Upper Silesia. The composition of the alum stone of different localities is shown by the following table:—

Locality	Tolfa		Hungary	Montioni	Mt. Dore
Analyst	Vauquelin	Klaproth	Klaproth	Descotils	Cordier
Sulphuric acid	25·0	16·5	12·50	35·6	27·0
Alumina	43·9	19·0	17·50	40·0	31·8
Potash	3·1	4·0	1·00	13·8	5·5
Water	4·0	3·0	5·00	10·6	3·7
Silica	24·0	56·5	62·25	—	28·4
Ferric oxide	—	—	—	—	1·4

It is evident from this table that the composition of alum stone varies, and its constitution has been represented by different formulæ; Cordier represents it as—

$$2Al_2 3SO_4 + K_2SO_4 + 5Al_2O_3 + 15H_2O.$$

Mitacherlich represents it as—

$$Al_2 3SO_4 + K_2SO_4 + 2Al_2O_3 + 12H_2O.$$

Ordinary alum stone is for the most part amorphous and of a reddish colour; the purer kind is white and crystalline. It is insoluble in water. When strongly heated it behaves like alum, but when heated only to a dull red heat, water dissolves out from it ordinary alum, while alumina remains behind—a result which may be understood by a glance at the formulæ representing the composition of alum stone. Hence the preparation of alum from this mineral is very simple; the alum stone being merely burnt, the calcined mass lixiviated with water, and the solution evaporated to crystallisation.

In burning alum stone great care must be taken that the heating is neither too great nor too little. When alum stone is insufficiently burnt it is not fully disintegrated, and if heated too much sulphuric acid is driven off, leaving an insoluble basic compound. The burning operation is generally judged to be complete when vapour containing sulphurous and sulphuric oxides begins to be given off. The operation is carried out either in reverberatory furnaces—as at Tolfa—where the alum stone is spread upon the hearth of the furnace, or in heaps—as at Civita Vecchia—in which case it is piled up in alternate layers with fuel, the heap being set fire to and the combustion regulated by draught holes.

After the alum stone has been roasted, it is gradually mixed with water into a paste, and lixiviated with hot water in large pans. The solution when sufficiently clear is drawn off, evaporated at a temperature of about 50° and allowed to cool and crystallise in vats, upon the sides of which alum deposits; the mother liquors yield by further evaporation cubic alum. The crystallisation is often carried out so that some cubic alum is deposited with the ordinary octahedral alum.

Alum prepared in the above manner is known as Roman alum.

Alum from Alum Slate and Alum Earth.—These alum ores consist chiefly of clay slates permeated throughout with finely divided iron pyrites as well as bitumen and carbonaceous substance. Some kinds of earthy brown coal are also regarded as alum ores. When materials of this kind are exposed for some time to the action of the atmosphere, a process of oxidation takes place by which the iron pyrites FeS_2 is converted into ferrous sulphate, basic ferric oxide and free sulphuric acid. The slower the oxidation the smaller is the amount of ferrous sulphate and the greater the amount of basic ferric sulphate and free sulphuric acid. The free sulphuric acid formed in this process acts upon the clay, forming aluminum sulphate and free silica. Upon lixiviating alum earth that has been thus altered, alum may be precipitated out from the solution by adding to it potassium sulphate, and on evaporation of the filtrate crystals of ferrous sulphate are obtained. According to the amount of aluminum sulphate or of ferrous sulphate in the oxidised earth depends its value for preparing alum or green vitriol. The following table gives the results of analyses of several different kinds of alum slates and earths.

	Alum Slate			Alum Earth	
Locality	Goslar	Whitby	Garnsdorff	Bornstädt	
Analyst	Frick	Richardson	Erdmann	H. Müller	
Silica	60·03	52·25	50·13	33·34	14·02
Alumina	14·91	18·75	10·73	18·73	9·65
Cupric oxide	0·28	—	—	—	—
Ferric oxide	8·94	—	2·27	—	—
Ferrous oxide	—	8·49	—	2·53	5·22
Lime	2·08	1·25	0·40	1·16	0·74
Magnesia	4·22	0·91	1·00	1·08	1·02
Potash	3·87	0·13	—	1·78	1·14
Soda	—	0·20	—	0·19	
Iron pyrites	—	4·20	7·53	2·75	19·27
Carbon	5·67	4·97	22·83	34·63	43·64
Hydrogen		—	—		
Nitrogen		—	—		
Water		2·68	2·21		
Sulphuric acid	—	1·37	—	0·27	0·67
Sulphur	—	—	—	2·65	1·87
Chlorine	—	traces	—	traces	0·10

Alum slate is often found near coal seams as at Whitby, at Hurlet, and Campsie in Scotland, at Saarbrücken, also in Saxony, Bohemia, Sweden and Norway, near Düsseldorf, and in the neighbourhood of Liége.

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Alum earth contains more carbonaceous material than alum slate, and it is generally associated with brown coal seams as in Brandenburg, and especially in the lower Oder district near Freienwalde, Gleissen, Schermeissel, etc., and in the neighbourhood of Muskau and the valley of the Mulde, where the alum works at Schwermsal, near Düben, are more than three centuries old.

The alum earth of Bornstädt, in the Mansfeld district, lies under the brown coal. Besides these sources, alum earth is found at Bonn, Neuwied, and in several parts of France and Austria.

Roasting of Alum Ores.—Various methods are adopted in roasting alum ore. Some kinds are sufficiently oxidised when exposed for some time to the action of the atmosphere; more frequently, however, the application of heat is requisite in order for complete oxidation. At Bornstädt both methods are combined; the alum earth is piled up upon large well-ventilated clay stages, in layers 6 or 7 feet in depth, and left for three years, a process of lixiviation being carried out each year, the specific gravity of the liquor after the first year being 1·125, the second year 1·091 to 1·108, and the third year 1·067 to 1·075. At the end of the third year the mass is piled up in heaps, which in a short time take fire spontaneously, and the ore is thus roasted by the combustion of its carbonaceous material, or if it does not contain a sufficient amount, some small coal or brushwood is added. The combustion is prevented from becoming so active at any part of the heap as to cause the formation of too much sulphurous acid, by covering the heap with earth or lixiviated ore.

As a rule, alum slate contains too little combustible material for burning it, and therefore in most places it is heaped up with alternate layers of fuel. The roasting heaps are made by covering a layer of brushwood, 110 feet long and from 6 to 10 feet wide, with a layer of 2 feet of alum slate. The brushwood is set fire to in the middle of the heap, and the combustion is promoted by small openings. When the combustion has extended sufficiently throughout the mass, a fresh quantity of brushwood is laid on, and upon it a layer of alum slate of the same proportions as before; these successive operations being continued until eight or ten layers of alum slate have been piled up; the last layer of alum slate requires to be very compact so as to keep out rain from the heap. The combustion must be conducted so slowly that some months elapse before it is complete.

According to Mohr's method, the roasting is carried out in shaft furnaces, and the ore is drawn out below, while fresh supplies are thrown in above, so that the process is continuous.

Laminne's method consists in passing through the roasting heap sulphurous oxide mixed with air and steam, the sulphurous oxide being a by-product of the roasting of metallic sulphides. By this method the yield of alum is said to be greatly increased.

Lixiviation of the Roasted Shale.—This operation is often conducted in vats or tanks arranged at different levels as in the extraction of soda from soda ash, so that a given quantity of water is made to act successively upon several portions of material. The liquor thus obtained is sometimes concentrated by evaporation, by running it over the surface of thorn faggots as in the preparation of salt. In any case, during the lixiviation a continual oxidation of the ferrous sulphate present in solution takes place, and insoluble ferric sulphate is deposited, The liquor, after having been left to settle, then contains chiefly aluminum sulphate, ferrous sulphate, together with alkaline sulphates and chlorides and free sulphuric acid. The concentration of the liquor is generally carried to such a degree that it has a density of from 1·09 to 1·15, but not more, since the muddy deposit would in that case retain some aluminum sulphate.

Boiling of the Liquor.—This is conducted differently according to the relative proportions of aluminum sulphate and ferrous sulphate. When the former preponderates, and the liquor contains but little ferrous sulphate, it is boiled down until it has a specific gravity of 1·357 to 1·41, and then by adding potassium chloride or potassium sulphate alum is precipitated from it. Sometimes the solution from which the alum has been separated is evaporated to obtain ferrous sulphate. When this is to be done the precipitation of alum must be effected by potassium sulphate, so as to avoid the conversion of the iron salt into chloride.

When the liquor contains much ferrous sulphate and but little aluminum sulphate, it is either evaporated until it has a specific gravity of 1·262 to 1·383 and then cooled, in order that the ferrous sulphate may crystallise out, or it is evaporated with constant addition of mother liquor from previous operations until it has a specific gravity of 1·357 to 1·383 and ferrous sulphate begins to be deposited in the boiling pans. In case the shale operated upon contains a sensible amount of potassium salts, the liquor is in the first instance evaporated just so far that alum crystallises out, and when this has been separated the boiling down is continued until greater part of the ferrous sulphate

has been deposited and the mother liquor can be treated with potassium sulphate for the purpose of precipitating alum.

The evaporating pans are either stone cisterns or leaden pans, and in some places the liquor is heated by passing flame and hot gas from a furnace over the surface, while in their places the pans are open and heated from below.

Precipitation of Alum.—The solution containing aluminum sulphate when sufficiently concentrated is first run into settling vats, and then into coolers, where it is mixed with a hot concentrated solution of potassium salt, the whole being well stirred meanwhile, so as to make the alum separate in a pulverulent form. It is requisite to avoid the formation of large crystals, because they would retain mother liquor, and be on that account less pure than the finely divided precipitate. The use of potassium chloride for precipitating the alum of course presupposes that the liquor contains other sulphates besides aluminum sulphate, and an amount sufficient to convert it into sulphate, for the formation of alum. The proportion of potassium salt to be used must be ascertained by special trials with small quantities of the liquor or by analysis and calculation.

The alum flour thus obtained is collected upon large wooden strainers, and washed by stirring it with water saturated with alum, so as to remove from the alum flour adhering ferrous sulphate. Centrifugal machines are also used for the purpose of washing the alum flour.

In order to obtain alum in the form of crystals, the flour is dissolved in hot water until the solution has a specific gravity of 1·498 to 1·530, and then it is run into tub-shaped wooden crystallising vats, where upon cooling it becomes almost entirely solid. When the crystallisation is complete the mother liquor is drawn off and the solid blocks of alum are taken out by removing the sides of the crystallising vats.

Uses.—Alum is used in dyeing and calico printing, as a mordant for fixing colours, also in the preparation of l a k e s or compounds of alumina with pigments, which are obtained by mixing extracts of dye stuffs with solution of alum and then precipitating the alumina. Alum is useful as a disinfectant, and when added in very small proportion to muddy water, it promotes the deposition of suspended material. It is used together with gelatin or resin soap for sizing paper. Alum combines with gelatin, and is therefore used in tanning leather. When added to melted lard or other kinds of animal fat, it promotes the separation of cellular substances and clears the fat: it is used in medicine as an astringent and caustic. Alum is also used for hardening gypsum casts and for colouring articles made of gold alloys.

AMMONIA ALUM.

Formula $AlNH_4(SO_4)_2 + 12H_2O$. Molecular Weight 453·5.

This salt is now largely employed in place of potassium alum; it has exactly the same appearance, the crystalline form is the same, and it has nearly the same solubility in water. When the solution is heated with caustic soda or lime, ammonia is disengaged. At a red heat the salt is decomposed, giving off water, ammonium sulphate, and sulphuric acid, while alumina remains. Poggiale gives the following quantities as representing the solubility of the salt at different temperatures:—

100 parts of water dissolve	5·22 parts	at a temperature of	0°
	9·16 ,,		10
	13·66 ,,		20
	19·29 ,,		30
	36·51 ,,		50
	71·97 ,,		70
	187·82 ,,		90
	421·90 ,,		100

Ammonia alum is prepared in the same manner as potassium alum, a concentrated solution of ammonium sulphate being substituted for the solution of potassium sulphate in precipitating the alum flour from the liquor containing aluminum sulphate.

SODIUM ALUM.

Formula $AlNa(SO_4)_2 + 12H_2O$. Molecular Weight 458·5.

This salt is much more soluble in water than potassium alum, and when its solution is boiled or heated for some length of time to a temperature above 60°, it becomes

uncrystallisable. It effloresces readily when exposed to the air. On account of its greater solubility it is more difficult to obtain it free from iron than potassium alum, and for this reason it is seldom used.

SODIUM ALUMINATE.

FORMULA $AlNa_3O_3$. MOLECULAR WEIGHT 144·5.

This substance has a composition analogous to that of aluminum trihydrate, hydrogen being replaced by sodium, as shown in the above formula. It is freely soluble in water, and is for many purposes a useful substitute for ordinary alum.

A solution of sodium aluminate, when mixed with a solution of aluminum chloride, gives a precipitate consisting of aluminum hydrate, according to the following equation:

$$2AlNa_3O_3 + Al_2Cl_6 + 6H_2O = 4AlH_3O_3 + 6NaCl.$$

Sodium aluminate is prepared by heating to redness a mixture of the aluminous mineral called bauxite and soda ash, until the sodium carbonate has been decomposed and a portion mixed with acid no longer effervesces. The mass is then lixiviated with water, the silica remaining undissolved separated by filtration, and the clear liquid evaporated to dryness. This substance may also be prepared from cryolite by the methods already described at page 270, and it is produced in the manufacture of soda according to Balard's method from sodium sulphate, bauxite, and carbon (p. 271).

Sodium aluminate is used for many of the purposes to which alum is applied; in dyeing and calico printing, for the preparation of lakes, for hardening stone, and in the saponification of fat in candle factories; in this case an insoluble aluminous soap is produced which is decomposed with acetic acid, yielding soluble aluminum acetate and fatty acid; it is also used in making an opalescent glass or kind of semi-porcelain.

Among the materials employed in the manufacture of utensils for culinary and other domestic uses, there are two which, from a chemical point of view, present great similarity, viz. clay and glass, inasmuch as they are both compounds of silica, chiefly with earthy or alkaline bases. The principles involved in the manufacture of glass and the various kinds of pottery ware are, likewise, so similar, that it is convenient to treat of these two branches of industry together.

GLASS.

History.—The discovery of glass is described by Pliny as having been the result of an accidental observation of certain Phœnician merchants, while heating a cauldron supported upon soda blocks on the sea-shore. According to this tradition, the melted soda formed glass with the sand beneath; but the story has little probability, and, moreover, modern research has clearly proved that the manufacture of glass was known at a period much earlier than that referred to by Pliny. Most probably glass was first made by the Egyptians, for some of their oldest works of art are partly made of glass, or ornamented with enamel. At a later epoch the trade in glass was almost entirely in the hands of the Phœnicians, and this may have given rise to the above-mentioned myth.

In early times the glass works at Thebes, Sidon, and Alexandria were very celebrated. The first among the Greeks who makes mention of glass is Aristophanes, in the fifth century before Christ. It appears to have been introduced into Italy about the time of Cicero; and during the reign of Tiberius a company of glass-blowers established themselves in Rome, where glass was soon afterwards very extensively in use. Fragments of glass have been found at Herculaneum that are very similar to modern window glass. The first mention of window glass proper is found in the works of Lactantius, written at the end of the third century. During the middle ages, Venice became famous for its glass manufacture, and this branch of industry exists there at the present day in the island of Moreno. From Venice, the secret of glass-making found its way into Bohemia, France, England, Sweden, and other countries. The exact date of the introduction of glass into Germany is not known, but it is probable that glass was made there earlier than in the neighbouring countries, although it did not attain great dimensions, owing to its having been carried on in small forest smelting houses, where the materials were cheap.

Coloured glass, the production of which admits of the use of less pure materials than colourless glas, was known at a much earlier period. According to Seneca,

the art of making artificial emeralds was discovered by Democritus of Abdera; other artificial precious stones were, however, known before the time of Democritus. The manufacture of coloured glass attained a high degree of perfection in Rome, and still more so in Venice, whence the art spread to other countries. In ancient times the art of glass painting consisted in connecting together pieces of differently coloured glass with strips of lead. At the present day the art is so perfected that it is possible to give different colours to the same plate of glass.

Composition.—Glass generally consists of a mixture of two or more silicates that have been united by fusion into a homogeneous, hard and brittle mass. The silicates which constitute ordinary glass are chiefly those of potassium, sodium, calcium, and lead; iron, zinc, manganese, barium, and aluminum silicates are also frequently present in small proportions, and some kinds of glass also contain borates. The following table gives the composition of different kinds of glass:—

	SiO_2	K_2O	Na_2O	CaO	PbO	MnO	Al_2O_3	Fe_2O_3	Analyst
Window glass, English	69·00	—	11·10	12·50	—	—	7·40	—	—
„ „ French	70·00	—	15·00	13·40	—	—	1·50	0·10	—
Plate „	75·90	—	17·50	3·80	—	—	2·80	—	Payen
„ „ Aix-la-Chapelle	78·75	—	13·00	6·50	—	—	1·75	—	Benrath
Bottle „ Bohemian	58·40	1·80	9·90	18·60	—	—	2·10	8·90	Maumene
Bohemian „	71·70	12·70	2·50	10·30	—	0·20	0·40	0·30	Berthier
„ „	76·00	15·00	—	8·00	—	—	1·00	—	Peligot
Plate „	67·70	21·10	—	9·90	—	—	1·40	—	„
Bottle „ Sèvres	53·55	5·48	—	29·22	—	—	6·01	5·74	Dumas
„ „ St. Etienne	60·00	3·10	—	23·30	—	1·20	8·00	4·00	Berthier
Optical „ German	62·80	22·10	—	12·50	—	—	2·60	—	Dumas
Crystal „ French	58·00	8·90	—	2·60	32·50	—	—	—	Payen
„ „ English	59·20	9·00	—	—	28·20	—	—	0·40	Berthier
„ „ „	51·90	13·70	—	—	33·30	—	—	—	Faraday
Optical „ Guinand's	42·50	11·70	—	0·50	43·50	1·00	1·80	—	Dumas

Characters.—Glass as ordinarily met with is a homogeneous mass possessing the peculiar texture characteristic of the alkaline silicates after they have been melted; it has also a peculiar lustre, and is usually transparent as well as colourless, unless it contains a large amount of metallic oxides which communicate to it colour and opacity. At ordinary temperatures it is hard and brittle; the fracture is conchoidal; in thin sheets or threads glass has some degree of flexibility; when heated to a sufficiently high temperature it becomes plastic and ductile. The characters of glass vary according to the particular nature as well as the relative proportions of the silicates it contains. The greater the amount of silica in glass, the less fusible it is; the greater the amount of alkali, the more fusible is the glass. The presence of a considerable amount of calcium silicate renders glass less readily fusible.

The specific gravity of different kinds of glass differs slightly, as shown in the following table by Dumas:

Bohemian glass	2·396
Crown glass	2·487
Mirror glass	2·488 to 2·506
Window glass	2·642
Bottle glass	2·732
Crystal or flint glass	2·900 to 3·255
Optical flint glass	3·300 to 3·600

When hot glass is rapidly cooled it becomes very brittle; this is especially the case when the pieces are thick, as the cooling then takes place very unequally, the outer parts cooling much more quickly than the interior. Glass in this condition is readily affected by change of weather, slight vibrations, etc., and is more apt to crack the more rapidly it has been cooled. When a drop of red-hot glass is allowed to fall into cold water, the surface cools very quickly, and becomes hard while the inner portion is still very hot, and consequently expanded. When the interior also cools, it cannot contract owing to the solidity of the outer surface. Glass drops thus prepared are known as Rupert's drops or devil's tears; they terminate in a fine thread, upon breaking which the entire drop explodes, and is converted into a fine powder. When the experiment is conducted in a glass vessel filled with water, and having a narrow mouth, the force of the explosion of the glass drop is sufficient to break the

glass vessel. This pulverisation is due to the unnatural and constrained arrangement of the glass particles, consequent upon the rapid cooling, and only a slight vibration is sufficient to effect their mutual repulsion. The so-called Bolognese flasks have a similar construction. These are small flasks with very thick sides that have been very rapidly cooled in the air; a grain of sand allowed to fall into one of these flasks is sufficient to cause it to crack with a slight report.

In order to render glass proof against rapid change of temperature, such as takes place when hot water is poured into a glass vessel, as well as the external influences, it must undergo a process of very slow cooling, which is called annealing.

A remarkable change in glass, through which it becomes dull, opaque, and porcelainlike, is termed devitrification. It takes place when glass is kept for a long time at a temperature near to its melting point, or when it is very slowly cooled; also on heating glass in the flame of a blowpipe, which is not sufficiently hot to melt the glass. This devitrification is probably due to the more fusible alkaline silicates melting at a temperature insufficient to fuse the more refractory silicates, which are consequently separated in a crystalline condition. The old theory that devitrification is due to the volatilisation of alkali has been refuted by the results of a number of researches.

A very curious phenomenon is that of the coloration by sunlight of certain kinds of glass; they acquire first a yellowish colour, which gradually changes to violet. This coloration is probably due to the presence in the glass of ferrous and manganous oxides, the first reaction consisting in the higher oxidation of the ferrous oxide, producing a yellow colour in the glass; the protracted action of light and air then oxidises the manganous oxide, the delicate violet colour of which blends with the yellow of the iron oxide, colouring the glass red; when still more manganese is present, the glass assumes a violet colour.

Hydrofluoric acid attacks all kinds of glass, decomposing the silicates of which it consists, and forming silicon fluoride, water, and fluorides of the metals contained in the glass. This property of hydrofluoric acid is taken advantage of industrially for glass engraving.

The resistance of glass to atmospheric and other influences decreases as the amount of alkali increases; glass containing a large amount of alkali readily loses its lustre and becomes cloudy; and it is more easily acted upon both by hot and cold water than glass which is rich in silica.

Atmospheric moisture is especially injurious to glass, the effect being in proportion to the greater amount of bases in the glass. This is often seen in window panes made of bad glass, which after a short time become dull, the effect being due to the separation of a very thin film of silica upon the surface of the glass, by the simultaneous action of atmospheric moisture and carbonic acid upon the silicate of which the glass consists, and it occurs with greater rapidity in proportion to the degree of moisture and heat to which the window is exposed; hence the windows of stables and hot-houses very quickly become dull. The action of water upon glass is manifested in an especially unpleasant manner in optical glasses containing a large amount of alkali. When glass of this kind, owing to its slightly hygroscopic nature, becomes coated with moisture, the water gradually decomposes the glass, rendering it dull, and, in course of time, useless.

The behaviour of glass towards boiling water, different acids and saline solutions, has been investigated by Emmerling. He found that the action of boiling solutions and boiling water upon glass is, within certain limits, proportional to the time. With new vessels it is somewhat greater at first (during the first hour) and diminishes with longer use. The action is also proportional to the amount of glass surface exposed to the boiling liquid.

The action of boiling liquids upon glass during a given time is independent of the amount of liquid evaporated. The action decreases with the decrease of temperature of the liquid. Glass is attacked by even small quantities of alkalies.

The action of most acids, especially in a dilute state, upon glass, is even less than that of water, but sulphuric acid is an exception to this rule, as it attacks glass more powerfully than water. Glass is acted upon, more powerfully than by water, by solutions of salts whose acids form insoluble calcium salts, such as sulphates, phosphates, carbonates, and oxalates, the action increasing with the concentration of the solutions. On the other hand, solutions of salts whose acids form soluble calcium salts, such as chlorides, or nitrates, etc., attack glass less strongly than water, the action decreasing with the concentration of the solutions.

Varieties of glass differing only slightly in their percentage composition have nearly an equal power of resistance. The Bohemian glass (potash glass) resists reagents, especially acids, better than soda glass. The constituents of glass dissolve in about the same ratio as they are contained in the glass.

The following table shows the quantity per hour of glass dissolved from flasks having a capacity of 600–700 c.c. by 400 c.c. of different solutions of salts, being the average of from 1 to 30 hours boiling. The glass taken for the experiment was from glass works near Great Rhuden in Hanover, and had the following percentage composition :—

Silica	73·79
Alumina	0·58
Zinc oxide	0·68
Manganous oxide	0·32
Lime	8·61
Magnesia	0·12
Soda	13·94
Potash	0·60

Solvent	Per cent.	Quantity of glass dissolved per hour
Water	—	0·0021–0·0022 gram
Dilute hydrochloric acid	11	0·00044–0·00029 „
Aqueous ammonia	9	0·0029–0·0033 „
Sulphuric acid	2·5	0·0038 „
„ „	5	0·0044 „
„ „	2·5	0·0036 „
Sodium carbonate	1	0·0329–0·0355 „
„ „	0·25	0·0171–0·0189 „
Caustic potash	0·25	0·0115 „
Potassium chloride	10	0·0014–0·0017 „
Sodium sulphate	2	0·0060 „

Preparation.—Glass is made by melting together various materials containing silica and the requisite basic oxides so as to form silicates, and while the mass is in a melted state it is worked into the different shapes requisite for the purposes to which it is to be applied. The materials used in making glass are the following:

Siliceous Materials.—The most convenient material to use as a source of silica for glass manufacture is sand, owing to the fine state of division in which it occurs. In the manufacture of ordinary glass any convenient river or sea sand may be used; but in the preparation of white glass only the purest sand can be used, such as is found in the Isle of Wight, near Lemgo in Germany, and at Fontainebleau in France. Such sand is, however, previous to use, freed from mechanical admixtures of clay, etc., by washing.

Both quartz and flint occur abundantly in certain districts in a sufficiently pure state for making glass; before being used, they require to be reduced to a fine state of division, an operation which is very tedious, owing to their hardness. It is effected by heating the materials to redness, and then cooling them in water. This gives rise to a number of small fissures, and by stamping and grinding the previously hard mass can then easily be reduced to a fine powder.

Infusorial earth, consisting of the siliceous remains of infusoria, is on account of its fine state of division and great purity very suitable for glass manufacture.

Benrath recommends the use of granite as the siliceous material for making glass. Experiments made by him with granite from quarries in Finnland, which contained 75 to 78 per cent. of silicic acid, 10 to 12 per cent. of alumina, and 4 to 6 per cent. of potash, yielded very good results.

Basic Materials.—In the manufacture of ordinary glass, crude potash is employed as the potassium constituent; but for the better kinds of glass, refined potash must be used. For the commonest sort of glass, wood ashes may be used.

Formerly, the soda used in the manufacture of glass was obtained by the incineration of land and marine plants, and known as kelp or varec. Afterwards the purer soda obtained by Leblanc's process was employed; it is used in the calcined state, and, according to the quality of glass required, more or less pure.

Since the beginning of the present century, sodium carbonate has been almost entirely replaced by sodium sulphate, or Glauber's salt, used in the calcined state. To this is added about 5 per cent. of powdered charcoal, which facilitates the volatilisation of the sulphuric acid, the reaction consisting in the reduction of sulphuric acid to sulphurous oxide, which escapes as gas. The formation of glass is accelerated by this process. In some places common salt is employed; in the manufacture of glass, but its decomposition is very slow and difficult. A better material is found in pan scales, or the scaly mass adhering to the cauldrons in which brine is evaporated.

It consists essentially of a mixture of gypsum, sodium chloride, and sodium sulphate. The best material for supplying calcium is chalk, which is used in the powdered condition. In the manufacture of common kinds of glass, the selection of the chalk is unimportant, but for glass of better quality, chalk free from ferrous carbonate must be used. In districts where chalk is scarce, ordinary limestone is used, either merely powdered, or, as in France, previously burnt and then reduced to a fine powder by exposure to the air. The lime ashes from soap works, consisting of calcium hydrate, calcium carbonate and potassium carbonate, or sodium carbonate, form a material very suitable for use in the manufacture of glass.

Calcium fluoride, a by-product obtained in the preparation of soda from cryolite, is from its ready fusibility very suitable for use in glass-making.

In French glass works, heavy spar is used in the state of powder. It is said to exert a very solvent action upon the sand, and yields a very homogeneous and easily fusible glass, which admits of being easily worked. Strontia has also been proposed as a constituent of glass.

In the preparation of crystal or flint glass and other kinds which contain lead as an essential constituent, red lead (Pb_3O_4) is used. It is decomposed upon melting into lead oxide and oxygen; the liberation of oxygen ensures the oxidation of any organic substances present, and thus prevents the reduction of the lead oxide to metallic lead. Litharge is less frequently used, since metallic lead is apt to be produced.

Zinc oxide is used in Belgian glass works. Wagner recommends the use of blende, and gives the following recipe for making zinc glass:

Glauber's salt	213 parts
Blende	48·6 ,,
Sand	205·1 ,,

Manganese peroxide is used in glass-making to neutralise the green colour caused by the presence of iron; it is therefore obvious that the manganese peroxide must be itself free from iron. Another purpose served by manganese peroxide is the oxidation of organic substance, thus preventing discoloration of the glass by carbon.

Felspar and other easily fusible silicates are but seldom used in the manufacture of glass, and only for glass of inferior quality; the same may be said of basalt and blast furnace slag, which are sometimes used in making bottle glass. In many places arsenous acid is used for oxidising organic substance by its decomposition into free oxygen and metallic arsenic which escapes as vapour.

The several raw materials used in making glass are now nearly always employed in a fine state of division. When necessary they are first of all stamped, then ground and passed through sieves; afterwards they are mixed together upon a smooth floor with shovels. The mixing is completed in an apparatus introduced by Chance, which consists of a wooden box with a round bottom, in which a roller furnished with stout projections is made to revolve. The mixture is introduced through a wooden hopper in the lid, and the thoroughly mixed powder is withdrawn through a trap at the bottom of the mixing box.

Bottle Glass.—The materials used in the manufacture of bottle glass differ very much. For green, yellow, brown and other coloured varieties, impure raw materials may be used, provided that the silica and the basic oxides are taken in correct proportions. If bottle glass contains too much alkali, it may be acted upon by acid liquids; if it contains too much silica, it is difficult to melt. To produce white bottle glass the materials must be very carefully selected. If perfectly colourless glass is required, potash must be used in place of soda, because soda glass always has a bluish-green tinge.

The following table shows the composition of mixtures for different kinds of bottle glass:

Green Bottle Glass.

Yellow sand	100	100	100	100	40
Fresh wood ashes	60–70	50	—	35	—
Exhausted ashes	160–170	—	—	165	—
Varec soda	30–40	200	—	35	—
Common salt	—	—	—	—	6
Glauber's salt	—	—	8	—	—
Chalk	—	—	10	—	8
Clay loam	80–100	80–100	—	80	—
Iron slag	—	—	—	—	50
Iron spar	—	—	—	—	80
Cullet (broken glass)	100	100	—	100	—

	Pale Coloured Bottle Glass.			*White Bottle Glass.*		
Sand	100	100	100	100	100	
Potash	50–60	30–35	50–60	41·5	54	
Lime	10–12	17	10–12	17·5	15	
Ashes	—	110–120	—	—	—	
Manganese	0·5	0·25–0·5	0·5	(?)	1	
Cullet	60–66	—	—	—	100	

Very frequently, however, in the mixture for white glass, and especially for pale coloured glass, the potash is partly or entirely replaced by soda.

Crystal or Flint Glass is a potash and lead glass, that may be considered as a double silicate of potassium and lead. Pure lead silicate has a yellowish colour, which disappears when melted with a sufficient quantity of potassium silicate. Bismuth might be substituted for lead, if it were not too costly. Recently, however, zinc has been brought into use in the place of lead.

Pure crystal glass is absolutely colourless, and refracts light more strongly than ordinary kinds of glass. Its specific gravity is between 2·900 and 3·255.

The materials used in the manufacture of crystal glass must be of the greatest purity. The silica must be perfectly free from ferric oxide and manganic oxide. It is, therefore, advisable in some instances to wash the sand with dilute hydrochloric acid before using it, then to remove the acid by means of water, and dry the sand at a red heat. Sometimes the sand is cleansed by washing several times with pure water, by which means the particles of clay are suspended and removed.

Usually, the potash undergoes purification by treating the crude potash with a small quantity of water, so that only the potassium carbonate is dissolved, whilst the potassium sulphate and other impurities remain undissolved; by evaporation of the water and calcination, the potash is again perfectly dried.

The lead oxide of commerce is scarcely ever sufficiently pure, as it contains cupric oxide, ferric oxide, and manganic oxide, which would impart colour to glass prepared with it. Generally, therefore, the lead oxide is prepared in the crystal glass factory itself by heating pure lead in a reverberatory furnace at a moderate temperature, and thus converting it into red lead (Pb_3O_4). The use of red lead has the great advantage that the oxygen liberated from it upon heating, oxidises any organic substance that may be present in the raw material of the glass mixture. This is so far essential that, by the removal of oxygen from lead oxide by organic matter, it would be reduced to metallic lead, and thus cause cloudiness in the glass. With the same object, the oxidation is in some manufactories effected by an addition of saltpetre.

The composition of the glass mixtures used in different crystal glass manufactories varies very much. In the following table some of them are placed side by side:

Sand	300	300	300	300	100	100
Red lead	200	200	215	180	70	60
Potash	100	90–95	110	120	30	20
Saltpetre	—	—	10	—	—	—
Borax	—	—	10	—	—	—
Glass cullet	300	100–200	—	300	—	—

To these mixtures is often added 0·45 of manganese peroxide or 0·60 of arsenous acid. Occasionally borax also is added; boracic acid, as before mentioned, increasing the brilliancy of the glass considerably.

Window and Sheet Glass.—Window glass, in respect to its composition, is of two kinds, potash glass and soda glass. The first, of which the manufacture was formerly general, contains potash as the basis of the glass mixture; the latter, soda. In countries where wood abounds, such as Bohemia, a considerable quantity of potash glass is still manufactured; but almost everywhere else soda glass is made.

Glass Mixtures for the Manufacture of Bohemian (Potash) Glass.

Powdered quartz	100	110	120	100
Purified potash	60	64	60	54
Chalk	20	24	25	15
Manganese	—	2	2	1
Saltpetre	2	—	2	—
Arsenous acid	0·5	0·5	0·5	—

To these materials is always added about as much broken glass (cullet) as the weight of powdered quartz, sometimes more, sometimes less.

Glass Mixtures for Soda Glass.

	Payen			Escautpont	Muspratt
Sand	100	100	100	50	560
Powdered quartz	—	—	—	50	—
Chalk	35	40	13	30	154
Soda	28	35	—	—	119
Sodium sulphate	—	—	58	40	63
Manganese	0·25	0·25	—	1·5	—
Arsenous acid	0·20	0·20	—	—	2
Charcoal	—	—	4·5	2·5	—
Broken glass	60	180	25	variable	448

It will be seen from the foregoing instances that the preparation of glass mixtures is exceedingly variable both as regards the ingredients and their proportions. According to the Report of the International Exhibition in London in the year 1862, the following glass mixtures are used in different countries:—

	England	Prussia	Bohemia	France	Russia
Sand	100	100	100	100	100
Limestone	38	—	—	—	—
Chalk	—	37	30	35	—
Sodium sulphate	28	34	—	36	—
Potash	—	—	—	—	20
Soda	—	5	24	—	—
Common salt	—	—	—	—	3
Powdered coke	1·3	2·25	—	1·75	—
Arsenous acid	1	1	1	1·25	—
Willow or elm ashes	—	—	—	—	40
Smalt	—	—	—	—	0·1

Plate Glass.—In making the thick sheets of glass used for mirrors and of late years also for windows and various other purposes, the materials are mixed in such proportions as to form a somewhat more fusible glass than that used in making ordinary sheet or window glass.

The thickness of the plate glass necessitates a very colourless material, and for this reason potash glass would be preferable, because of its greater freedom from colour. But soda glass is used, since it is more fusible and, therefore, better adapted for clearing and casting, great care being taken in the selection of the raw materials. In making very thick plates, for mirrors especially, great care must be exercised to produce the whitest glass possible, because any colour in the glass becomes more manifest with the increased thickness of the plate. Plates of a medium size are made from one sixth to one half an inch in thickness, but very large plates are made thicker still.

The thickness of the larger plates especially increases the danger of the occurrence of waves, knots, clouds, etc. in the glass. These flaws only become apparent when the manufacture is advanced comparatively far, and considerable cost has been incurred; all that can be done then is to cut the better portions into smaller plates. It is particularly for the avoidance of such flaws that soda glass, as an easily fusible glass, is used; and as the fusibility augments with the amount of soda, this is carried as far as possible, without rendering the glass hygroscopic, and consequently liable in the course of time to become dull on the surface.

Ordinary soda is used for the most part, but in many cases sodium sulphate or Glauber's salt and charcoal are also added.

For Mirror Glass.

	I.	II.	III.
Sand	300	100	100
Soda	100	—	33
Glauber's salt	—	39	—
Lime (pulverised in the air)	43	—	14
Limestone	—	39	—
Manganese peroxide	0·5	—	—
Arsenic	—	0·4	—
Wood charcoal	—	2·5	—
Broken glass	300	—	100

Optical Glass.—This is a finer kind of lead glass, which is principally used for

optical purposes. It should therefore be as as colourless possible, and free from waves, cloudiness, or air-bubbles. Its specific gravity is from 3·3 to 3·6.

Flint glass in moderately large pieces, free from flaw, and suitable for optical purposes, was for a long time a desideratum. It was first obtained by Guinand, and the manufacture was considerably improved by his successor Bontemps.

The glass mixture used by Bontemps gives a glass having a specifi gravity of 3·6, and has the following composition:

Sand	300
Red lead	300
Potash	90
Guinand added to the foregoing mixture:	
Borax	5·5
Saltpetre	4
Arsenous acid	1
Manganese peroxide	1

The lenses of telescopes and other optical instruments consist of a combination of two kinds of glass. Flint glass is highly refractive, but as the different rays are variously refracted, the resulting image is coloured at the edges. For the removal of this dispersion, crown glass is combined with flint glass and an image is thus obtained with sharp uncoloured edges.

The manufacture of optical crown glass is conducted essentially in the same way as that of flint glass; but on account of the greater heat required, it is still more difficult. The mixture used by Bontemps consisted of—

Sand	120 parts
Potash	35 „
Soda	20 „
Chalk	15 „
Arsenous acid	1 „

Coloured Glass.—Glass is coloured for different purposes, as, for instance, the preparation of artificial precious stones, coloured sheet glass, bottle glass, etc. In making artificial gems an extra pure glass, called strass, is prepared with powdered rock crystal, and pure potassium carbonate or caustic potash, and red lead that is perfectly free from copper, iron, or manganese. Borax is also usually added in the preparation of strass, but it must previously be purified by repeated recrystallisations. The following is a mixture for the production of strass: —

Rock crystal	300
Red lead	470–460
Caustic potash	163–168
Borax	22–18
Arsenous acid	1–0·5

The materials are finely powdered, thoroughly mixed, and melted in porcelain, or Hessian crucibles.

Amethyst is obtained by the addition of a small quantity of manganic oxide, cobalt oxide, and purple of Cassius.

Emerald by the addition of a little cupric oxide and chromic oxide.

Ruby by the addition of manganic oxide.

Topaz by the addition of antimony glass and a very little purple of Cassius.

Sapphire by the addition of smalt.

These materials, as well as the strass, are very finely powdered, thoroughly mixed and melted together.

The production of variously coloured sheet and bottle glass is carried out according to different methods. The glass is either coloured throughout the entire mass when it is made, or in working the glass by the usual methods a thin layer of coloured glass is extended over one surface by an operation that is called flashing and caseing. When the glass is coloured throughout, the colouring materials are melted together with the glass in the ordinary manner.

Red glass can be prepared by adding cuprous oxide to the glass metal; generally copper scale is used, a small quantity of soot or iron filings being added to reduce any cupric oxide present, the green colour of which would injure the red colour of the glass. Cuprous oxide glass is mostly used as a coating, because it would be too dark and opaque in a mass. The finest red, however, is obtained by the use of a gold solution, or the purple of Cassius; a solution of gold in aqua regia, or gold chloride can also be used.

The following mixture is given by Muspratt and Stohmann:—

Sand	20
Red lead	16
Hungarian potash	2
Saltpetre	2·5

Of this mixture 20 parts are mixed and melted with—

Borax	1·56
Tin oxide	·12
Antimony oxide	·12
Gold solution	sufficient to produce the colour required.

Yellow glass is obtained by adding charcoal to the glass mixture, and a finer colour by means of glass of antimony. But the finest yellow is produced by covering the glass to be coloured with a mixture of clay and silver chloride, and heating it in a muffle. A fine greenish-yellow coloured glass is obtained by the addition of uranium oxide to the metal.

Blue glass is obtained by adding cobalt oxide, in the shape of smalt.

Green glass is made by adding chromic oxide or cupric oxide; a less beautiful colour is produced by ferrous salts. The colour of bottle glass is due to the latter.

Violet glass is obtained by manganic oxide; with a blue shade by manganic oxide and a little smalt.

Black glass is only known in the opaque condition; it is produced by the addition of ferrous oxide, or cuprous oxide and smalt.

Opaque white glass is obtained by the addition of bone ash to colourless glass. The lime phosphate is not dissolved, but remains suspended in the metal, rendering the glass opaque.

Alabaster glass is prepared with a very small addition of bone ash. It differs from ordinary opaque white glass in containing an excess of silica.

In American, Bohemian, and Silesian manufactories, cryolite glass has been prepared for some years. Benrath uses for this purpose a glass mixture of 1 part of cryolite and 2 parts of sand.

Glass Painting.—Formerly coloured glass windows were made by setting pieces of differently coloured glass in the manner of mosaic-work by means of lead, the shading being effected with colour on the back. Afterwards uncoloured glass was painted as in ordinary painting. The colours used are metallic oxides, cobalt oxide, chromic oxide, etc., which are mixed with an easily fusible glass, painted with turpentine upon the glass surface, and then melted by heat, or fired. Of course, as the under layer should not be softened, the flux should melt before this happens and consequently it must be more easily fusible.

A glass having the following composition can be used as a flux:—

Powdered quartz	20
Lead oxide	25
Bismuth oxide	10

Should the colours be attacked by the lead or bismuth oxide, the following mixture may be used:—

Powdered quartz	20
Borax	15
Saltpetre	2·5
Calcium carbonate	2·5

In melting glass mixture a certain proportion of broken pieces of glass, or cullet, is added to it. This glass refuse is always at hand in glass works. The glass which has run out of the furnace from broken crucibles is also used in like manner as a flux. By this means the refuse glass is not only turned to account, but its addition to the glass composition facilitates vitrification, since this glass melts at a lower temperature than the composition and thus exerts a solvent action upon it.

The melting pots used for making glass are large crucibles, made of the most difficultly fusible fire clay, which must not contain more than mere traces of iron or lime; one of the best kinds of clay for the purpose is Stourbridge clay. In making glass pots, the clay is always mixed with a quantity of pieces of broken melting pots in a fine state of division, and kneaded up into a paste with water, and moulded with the hands into the desired shape. Before new melting pots are used, chips of broken glass are melted in them, so as to form on the surface a difficultly fusible glaze, techni-

cally termed lining, which helps to prevent the clay from being afterwards acted upon by the glass mixture.

The size of the melting pots depends upon the size of the furnace. In this country they are larger than in Germany. They differ also in shape, the section being round or elliptical; in this country they are wider above than beneath (4 to 5 feet above, and at the most 3½ feet below). They are generally open above; but those used for lead glass are covered with an arched top, as shown in fig. 182, and for charging and taking out the glass they are furnished with a muffle-shaped opening (A) at the side. The arched cover serves to protect the lead oxide from the reducing influence of the hot air of the furnace.



Fig. 182.

Figs. 183, 184, and 185, represent Siemens' glass melting pots, in the construction of which advantage is taken of the fact that, as the glass mixture approaches complete fusion, it becomes specifically heavier. To provide for the separation of the metal in different stages of the melting, these pots, of which figs. 183 and 185 show the vertical section, and fig. 184 the horizontal section, consist of three compartments communicating with each other. A is the melting compartment, B the space where the settling takes place, and C the working space, from which portions of the melted glass are taken out through

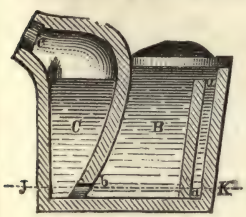


Fig. 183.

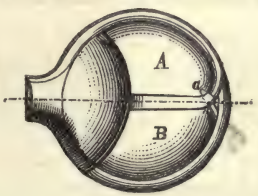


Fig. 184.



Fig. 185.

the opening (*c*) for working. The compartment (A) is filled with the glass mixture, and as this fuses and the molten mass increases in density, it sinks to the bottom, and passes through the opening (*a*) into the second compartment (B), where again the heaviest portion, corresponding with that nearest to complete fusion, sinks to the bottom, and passes through the opening (*b*) into the working space (c).

The furnace in which the glass pots are heated is in all cases a capacious vaulted chamber substantially constructed of refractory stone or fire bricks upon a solid foundation and over an arched passage called the cave, which is beneath the floor level and, extending from side to side of the furnace, serves to receive the ashes from the fireplaces as well as any portions of melted glass that escape from cracked glass pots. The fire grates are placed at the level of the floor over the cave as shown in fig. 187, and at the sides of the furnace are several arches by which access to the interior of the furnace can be obtained for setting the melting pots and when repairs are needed. The furnace is generally placed in the centre of a building called the glass house, in which the various operations of working up the glass are carried out, and the hot gas and smoke from the fire escapes either through flues at the side of the furnace, as shown in figs. 189 and 192, or into a conical tower built up round the furnace to a sufficient height to cause a draught.

The hot gas from the melting furnace is sometimes drawn off through side openings and conducted by flues to adjoining chambers which serve for fritting, calcining, drying and annealing, or for drying the glass pots.

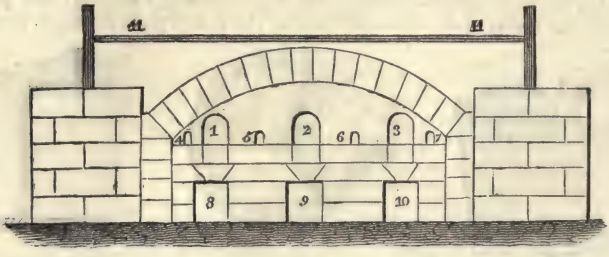
Glass furnaces are sometimes made large enough to contain eight or ten melting pots and sometimes they have only four pots. In various other respects also the construction of glass furnaces presents minor differences according to the nature of the work to be done.

The furnaces employed in making glass require to be very carefully built, both in order to produce the necessary temperature and to resist its influence for a considerable length of time. In their construction fire brick alone is employed. The bricks are laid with a very thin layer of fire-clay paste between the joints. In spite of all precautions, however, the sides of the furnaces are so much acted upon by the heat and the volatilised alkalies, that they are worn out and require rebuilding within 12 months, or sometimes within 6 months. Furnaces in which the more easily fusible lead glass is melted last proportionately longer than those in which the more

refractory kinds of glass are prepared. When the composition of the fire brick is defective the furnace has to be put out of use immediately, otherwise drops of melted silicates fall into the glass pots, where they either dissolve and colour the metal, or remain undissolved and form knots.

The interior or melting space of a glass furnace is either round, square, or elliptical, and it is heated either by a fireplace in the centre, or, according to the size of the space to be heated, by fireplaces at both ends or at one side only. Figs. 186 and 187 represent the elevation and horizontal section of a furnace for making crown-glass. On both sides of the melting space or all round it is an elevation, technically termed the bank, upon which the melting pots (1, 2, 3, 4, 5, 6, fig. 187) are placed, 4, 6, or 10 of these being placed in the furnace at one time. The melting space is arched above so as to concentrate the heat upon the melting pots. Above each pot is an aperture (1, 2, 3) in the side of the furnace for charging the pots as well as for withdrawing the glass when melted, and 4, 5, 6, 7 are pipe holes for warming the pipes before beginning to work the glass. Beneath the working holes are small tunnels (8, 9, 10), through which the melting pots can be removed when worn out, and replaced by fresh ones; these tunnels are built up when the furnace is in use.

Fig. 186.



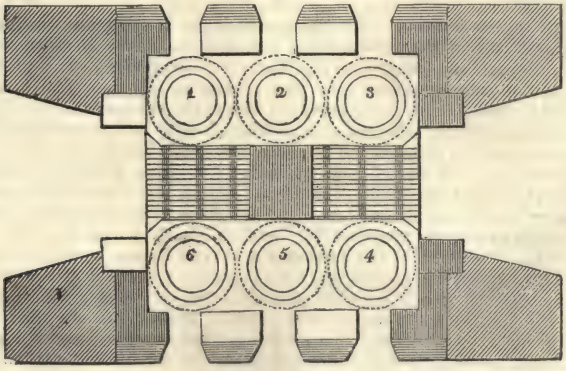


Fig. 187.

In consequence of the high temperature requisite for melting the materials in making glass—about 12,000°—and the necessity of maintaining the furnace at a high temperature while the glass is being worked, the consumption of fuel is very considerable, and there is in this case, as in all others where very high temperatures are necessary, a large quantity of heat carried off in the gaseous products of combustion which escape from glass furnaces. This heat is sometimes turned to account for heating the kilns or ovens in which the glass is annealed after it has been shaped, and several other plans have been devised for economising the heat produced in the glass furnaces and reducing the consumption of fuel. Among these may be mentioned the application of Siemens' regenerative furnace, which is furnished with two masses of brickwork arranged in such a manner that, while the hot gas from the furnace passes through one compartment, the supply of air to the furnace passes through the other compartment. By this means much of the heat in the waste gas is absorbed by the brickwork, and when this has become red hot the direction of the current is changed

by shutting and opening valves, so that the supply of air to the furnace is made to pass through the heated brickwork and acquire a high temperature before entering the furnace, while the other compartment is being heated by the waste products of combustion. The heat which would otherwise be wasted is thus to some extent again made useful for maintaining the temperature of the furnace, and there is a proportionate reduction in the amount of fuel consumed.

In Belford's furnace, represented by fig. 188, the fuel is used in the state of gas; on each side of the melting space where the glass pots (c c c c) stand upon the bank (G) are the chambers (D D) in which the coal is subjected to the action of a blast forced in through the tube (F) and the branch tubes (F′ F′), so that the coal is made to furnish combustible gas, partly by distillation, and partly by the formation of carbonic oxide, This gas flows through the openings (*d d*) into the melting space, and burns there on coming into contact with air supplied by the blast through the tubes (H H) and heated by passing through the chambers (J J), into which the heated air of the melting space passes through the openings (*g g*). The supply of this air is regulated by valves (*j j*). One advantage presented by this furnace is that the glass metal is not contaminated by the floating ashes, etc. from the fires.

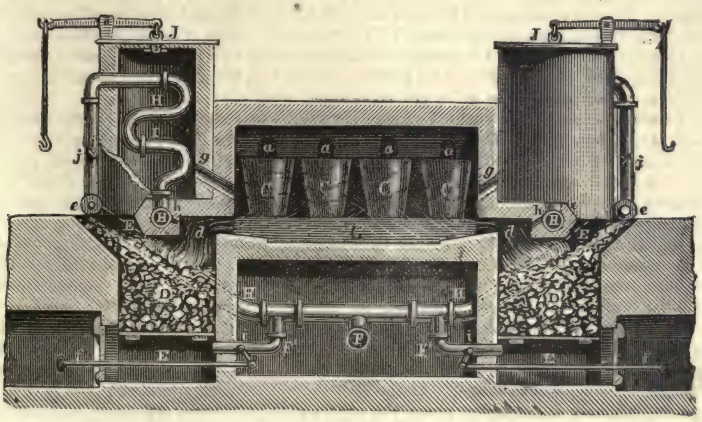


FIG. 188.

The reactions which take place in the melting of the glass materials are very simple. When silica is melted with alkaline or earthy carbonates, the silica displaces carbonic acid and combines with the basic oxides, forming silicates. A similar change takes place when red lead is mixed with the alkali, lead silicates being also formed by the decomposition of the red lead. During this process a considerable evolution of gas takes place, which is the cause of the bubbles so often observed in glass vessels. These bubbles may be expelled by heating the melted mass until it passes into a mobile liquid condition. Veins and streaks in glass are caused by the density of the melted mass not being homogeneous throughout.

A source of great inconvenience in the manufacture of glass is the volatilisation of alkali, which takes place before vitrification, *i.e.* before the alkalies have combined with the silica. When impure alkali or alkaline salts are used, a higher temperature is requisite and greater volatilisation takes place. The presence of chlorides, and especially of sulphates, gives rise to opaque threads and knots in the glass, which are caused by the melting of these salts in various parts of the mass without mixing with it. The volatilised alkalies condense upon the vault of the furnace, forming with the stonework impure silicates which melt and drop into the crucibles beneath, rendering the glass impure.

A further inconvenience attending the use of pots in making glass consists in the solvent action exerted upon the material of the pots by the melting alkalies, which not only renders the glass impure by dissolving alumina and iron, but is also very destructive to the pots.

Both the volatilisation of alkali and the solvent action exerted by the alkalies upon the melting pots must be taken into account in the mixing of the glass materials, and a corresponding extra quantity of alkali added.

The separate constituents of the glass having been calcined, the proper quantites are weighed out, and thoroughly mixed together. Sometimes only a portion

of the silica, with an excess of the bases, is melted with the broken glass, in order to fix the bases quickly; otherwise these being the first to melt, they would be volatilised in greater quantity, and afterwards the remainder of the materials, containing relatively less bases, is added. In any case, considerable loss of alkali cannot be avoided; amounting, with potash, ordinarily to 16 or 17 per cent., but frequently exceeding 25 per cent. The mixed materials are heated, generally in side ovens, seldom in special furnaces, to a red heat, or sometimes even until they commence to act upon each other, and the mass becomes pasty or *fritted*. Meanwhile new melting pots that have been previously heated to a red heat are introduced into the melting furnace through the crucible holes, which are then bricked up. The heat is then increased, and the glass material is introduced, in several portions, into the melting pots through the working holes. The heat is again increased to the utmost, in order to thoroughly melt and combine the silica with the basic oxides, the carbon dioxide and other acid oxides, previously in combination with them, being displaced and driven off. Foreign salts, such as potassium chloride and sulphate, which are decomposed very slowly or not at all, collect at the surface as scum or *gall*, and those that are not volatilised at the high temperature are skimmed off. The formation of *glass gall* is therefore due to impurities in the soda or potash. The temperature is now reduced until by the disappearance of the gas bubbles and the deposit of other impurities the metal has become completely clear. This clear melted glass is called *metal*, but being too thin to be worked, the temperature of the furnace is still further reduced. The glass when ready for working should be perfectly clear and transparent, and contain no air bubbles, or portions of the salts, grains of sand, etc.

In working glass into various shapes advantage is taken of the plastic condition it acquires when sufficiently heated, and in most instances this is done by forcing air into a lump of the glass sufficiently large to make the article required, so as to form a hollow globe which is afterwards shaped by various devices. This operation is termed *glass-blowing*, and the principal instrument used in carrying it out is an iron tube about an inch in diameter, and four or five feet long called the *pipe*. At one end there is a knob which serves as a mouth-pipe for blowing through the pipe, at the other end is a knob upon which the soft metal is taken up out of the glass pot, and part of the tube is sometimes cased with wood or other non-conducting material, so as to enable the workman to handle it more conveniently. When the lump of metal has been taken up on the pipe it is kept in a globular shape by rotating the pipe and rolling the metal upon the *marver*, which is either a smooth iron plate or a moistened block of wood which has several concavities in which the ball of metal is rolled to bring it into shape. At the same time the workman blows gently into the pipe and slightly distends the glass, the object being to obtain uniform distribution of the metal round the axis of the pipe before it cools so far as to require reheating. The further shaping of the glass globe after it has been heated at one of the working holes of the furnace is effected either entirely by blowing, or in part also by moulding the glass externally while air is forced in through the pipe.

This method of working glass is adopted not only for making bottles and various domestic utensils, but also for making sheet glass for windows, etc. The thicker kinds of sheet glass are, however, mostly made by casting and rolling the soft metal between a heated metal plate and a roller. Some articles are also cast or pressed into moulds.

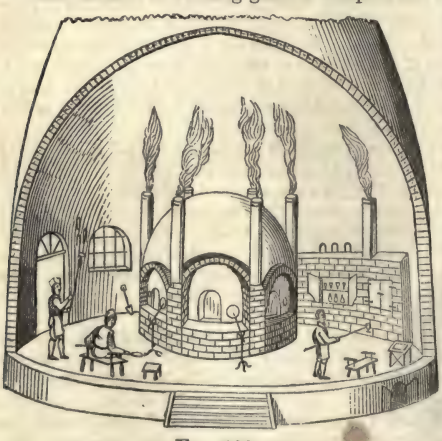


Fig. 189.

Blown Glass.—Bottles, drinking glasses, and other small articles are always blown, and the glass used for the purpose is either lime glass or flint glass. The arrangement of a glass house for making bottles, etc. is represented by fig. 189.

In the manufacture of bottles the pipe is the principal tool. Having taken out a sufficient quantity of glass for a bottle, the blower first works it to the front of his pipe, with a flat iron, blowing into it occasionally, and then rolling it in one of the depressions of the *marver*, so as to

form it into a slightly elongated globe. This is again heated in the furnace and lengthened by swinging the pipe backwards and forwards, after which it is put into a cylindrical mould, and blown out so that, whilst the colder neck is drawn out without being dilated, the body acquires the right diameter and height. The bottom of the bottle is then warmed, and pressed inwards with an iron rod in the direction of the axis, in order to produce the usual cavity, and an even edge upon which to stand the bottle. A second iron called the ponty is then attached by means of a piece of glass to the cavity in the bottom, the neck is separated from the pipe, and the bottle is held at the furnace mouth in order to melt the sharp edges, and to lay some threads of molten glass round the mouth to strengthen it. The neck is then levelled on the outside and enlarged cylindrically from the inside, with a pair of shears. The bottle joined to the iron is now carried by a boy to the annealing oven, where by a slight blow it is separated from the iron. Sometimes a complete mould in several parts is used, in which the bottles are rapidly blown, and thus a uniformity of size and shape is obtained that is otherwise only approximated to, notwithstanding the skill of the workman.

The annealing ovens for blown glass ware are either at the side of the melting furnaces and heated by the hot gas passing off from the melting furnace, or there are special annealing kilns heated by separate fires, as shown in fig. 189, and the bottles are allowed to remain there until they acquire the temperature of the oven. In England a continuously acting annealing oven is used. It consists of a long arched chamber, heated by a separate furnace. Wheeled trays run on rails from end to end. These trays are packed with the bottles to be cooled and slowly pushed from the hotter end of the chamber to the cooler end, by which time the bottles become sufficiently cool to be taken out. Instead of the trays an endless chain passing through the oven may be used, and the articles to be cooled are placed on the chain in boxes or trays.

Good bottles must not only withstand ordinary changes of temperature, but frequently, as in the case of champagne and soda-water bottles, they must be strong enough to sustain a considerable pressure from the inside; and to ensure this the glass must be of equal thickness throughout, and well annealed. In order to avoid loss by the bursting of champagne bottles, each bottle is proved separately before being filled, by pumping water into it under a pressure of twelve atmospheres.

In blowing very large round bottles, such as sulphuric acid carboys, the blower with his mouth spirts some water into the partly blown sphere of glass through the pipe, which he then closes with his thumb, and the vaporisation of the water serves to blow out the glass.

In making the finer kinds of blown glass articles lead glass is generally used, and in order to avoid the reduction of the lead oxide in the preparation of the metal, the glass pots are always closed above, so that reducing gases and coal dust are prevented from coming into contact with the molten metal, and they have also a kind of muffle-shaped opening at the side which fits into the working hole of the furnace.

After the raw materials have been thoroughly mixed, successive small portions are thrown into the glass pots and brought to the melting point as quickly as possible. Whilst the melting is going on the openings in the glass pots are closed. About 14 hours are required for the complete fusion of the metal, and about the same time for working up the metal of a pot containing about 6 cwts.

Crystal glass being more easily fusible than ordinary glass, it is more easily worked and can be more frequently reheated without becoming devitrified, provided that the flame does not exercise a reducing action upon it. It is worked into shape by means of the blowpipe, like ordinary glass; or by blowing it into metal moulds, for bottles and similar articles; or, lastly, by pressing it into metal moulds, for dishes, plates, etc. The glass obtained by blowing or pressing into moulds resembles cut glass and is much cheaper, but from the rapid cooling of the metal it is not sufficiently fluid to fill the mould perfectly, and therefore has not the sharp edges and angles of cut glass.

The softness, great density, and strong refracting power of crystal glass render it especially suitable for cutting. This is effected by pressing it against acute or obtuse-angled wheels driven rapidly by means of a belt. The glass-cutter's work may therefore best be compared with that of the turner inverted. The wheels as well as the grinding powders are changed at different stages of the cutting. The glass is first roughly ground with an iron wheel and sand and water; then follows a fine grinding with a sandstone wheel. The glass is then polished by means of a wooden wheel and pumice stone, and lastly by a cork wheel and tin oxide.

In the manufacture of coated glass the workman takes a small quantity of the coloured glass metal on his pipe, blows it slightly, and then dips the pipe in the pot containing the colourless metal, gathers as much as is necessary, and then blows it, etc. In this manner a hollow glass, coloured on the inside, is obtained, specially suited for cutting, since the grinding being carried out on the colourless exterior, the coloured

inner layer remains of equal thickness and depth of colour. If the glass is not to be ground the operation may be reversed, first the white and then the coloured metal being gathered with the pipe.

In this country a covering of coloured glass is first blown; this is opened at the top and colourless metal introduced on the pipe through the opening, and carefully blown so as to form a uniform layer on the interior.

In Bohemia small pieces of coloured glass are heated almost to melting on an iron rod in the working spaces, then laid on some colourless glass attached to a pipe, spread out evenly by means of the iron rod, and finally the whole is blown.

Crown or Moon Glass.—The manufacture of this kind of glass is extremely difficult, and is attended with considerable loss. The workman, having by repeated dippings of his pipe into the glass pot gathered a sufficient quantity of the metal, first forms it by blowing and rolling it on the marver; till it takes the forms I, K, L, fig. 190. This is again heated at the circular opening in the furnace, and the pipe is rapidly rotated, so that the bottom of the ball is flattened and forms a circular disc, as shown at M. To the middle of this disc, the ponty is soldered by means of a small quantity of glass, and the bulb is then separated from the pipe by breaking the neck across with a cold iron. The opening thus made is heated, by holding the bulb opposite the circular opening in the furnace, the ponty meanwhile being continually rotated, and the hole slightly widened by a wooden stick so that the bulb acquires the form shown at N. It is then carried to the flashing furnace, fig. 191, and heated opposite the opening (A) from which the flame issues and comes in contact with the bulb. The ponty is then rested horizontally on an iron bar, so as to expose the mouth of the bulb to the flame issuing from the round aperture (A), and very rapidly rotated. Through the influence of centrifugal force the edges of the hole widen, as shown at O, and presently a disk is formed, which is thick in the middle, where the ponty is attached, but elsewhere is tolerably uniform. This operation is called flashing, and the mode in which it is conducted is represented by fig. 192. When the disk has been formed and become sufficiently cool, it is laid upon a bed of hot ashes, separated from the ponty, and then removed by means of a fork-shaped iron into the annealing oven at the side of the flashing furnace, where it is placed on edge. The disk being cut, in order to remove the thicker part from the centre, two half-moon-shaped portions are obtained; hence, its German name of moon glass. It is evident that in the cutting up of these disks into regular panes of glass there must be considerable waste; it is on that account much more costly than the sheet glass made from cylinders.



Fig. 190.

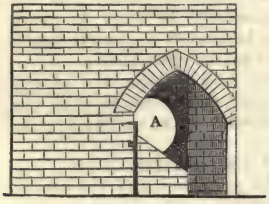


Fig. 191.


Fig. 192.

Cylinder or Sheet Glass.—At the present time window glass is almost universally prepared from cylinders obtained by manipulation of the metal with the blow-pipe. When the glass has cleared and been skimmed, the workman, having heated his pipe, gathers with it some glass from the pot and then turns it so that the metal congeals without running off; the pipe is then dipped in again, and the operation repeated until a sufficient quantity of metal is gathered on the end of the pipe, proportionate to the size and thickness of the cylinder to be made. When sufficient metal is attached to the pipe, the workman blows into it through the pipe, again heats it at the working hole, and while holding the lump of glass in the moistened cavity of a wooden block blows more air into it until the glass gradually takes the form of a pear-shaped bulb (A, B, C, D, fig. 193). He then holds the pipe vertically with the glass under-

neath, and swings it to and fro like a pendulum in a pit at the side of the working space, called the swinging pit, still blowing into the pipe from time to time. The glass thus gradually assumes the form of a cylinder (E F, fig. 193). It is necessary during this operation to keep the soft glass continually in motion or it would become unequally distributed. When the glass has been blown out to the required size, the workman supports his pipe upon a portable rest, and puts the cylinder into the working space of the furnace, so that the lower closed end of it may become heated. He then closes the pipe with his thumb, and the expansion of the enclosed air by the heat causes the softened bottom of the cylinder to swell out and finally burst. By rapidly turning the pipe backwards and forwards, this opening is widened; the cylinder is then taken out, and revolved, and swung to and fro until the opening has the full width of the cylinder (G, fig. 193). When the glass is so far cooled as to retain its shape without being swung, the cylinder is laid upon a rest, and a drop of water is applied with an iron to the upper end, where it is attached to the pipe; and then upon striking the pipe about the centre with an iron bar the cylinder separates. If the cylinder be of thick glass, it is cooled very slowly in proper cooling ovens; but with very thin glass this operation is superfluous.



FIG. 193.

The next step is to break off the conical end of the cylinder (the neck or cap), as shown at H, which is effected by encircling it at the place where it is to be separated with a red-hot thread of glass, or holding against it a red-hot circular iron called the springing iron, and afterwards touching the heated place with the moistened finger, or throwing a few drops of water upon it. The detached cylinder is then opened or slit lengthways, and for this purpose the workman draws the sharp edge of the iron in a straight line to and fro along the inner side of the cylinder, and then, by merely scratching with a pointed stone along the line thus heated, the cylinder cracks from one end to the other, the result being shown at H, fig. 193.

The flattening of the opened cylinder is carried out in an oven which consists of two parts, the flattening oven and the cooling or annealing oven. Within the oven is the flattening bed, which is a perfectly level surface made of fire clay and cement. In order to prevent the glass adhering to this surface some lime or ground gypsum is thrown into the furnace, so that the flame carries the powder forward into the oven and deposits it in a fine layer upon the flattening surface. The flattening oven is connected by an opening with the cooling oven, which contains a similar flat surface. When a cylinder is to be flattened, it is passed with the openings upwards, through the passage into the flattening oven, and gradually pushed forward towards the flatting space. As the cylinder advances into the oven it becomes heated by the hot gas from the fire, and it arrives at the flatting plate in a softened condition. The cylinder is then spread out by the workman by means of the flattening iron, with which he presses the glass outwards at each side of the crack until it forms a flat sheet; the polisher is then passed over it to render it perfectly even, and it is pushed forward by means of the flattening iron through the opening into the cooling oven, where it soon becomes sufficiently cooled to allow of its being set up on edge against iron rods. This operation is repeated upon fresh cylinders until the cooling oven is full, when it is closed in order to allow the cooling of the plates of glass to take place gradually.

Corrugated sheet glass is obtained by blowing out the cylinder in a ribbed bronze mould, the corrugations remaining even after the flattening.

In order to avoid loss in the transfer of the sheets of glass from the flatting stone to the cooling oven, Kirn has suggested a contrivance that presents decided advantages. It consists of two very thin flatting stones, arranged one over the other, which can be passed alternately from the flattening oven into the cooling oven. The glass cylinder having been flattened on one of the plates in the flattening oven, is carried forward on it into the cooling oven, allowed to cool and set upon edge. Meanwhile, another cylinder is being spread out on the second flatting stone in the flattening oven.

The flattening oven of Chance is constructed on a new principle. It consists of two domed chambers, standing side by side, and communicating through an opening. The hearth of each oven has a circular basis, and can be moved in a rotary direction by special machinery. Each oven is divided by radiating partitions into eight compartments, each compartment in the flatting oven containing a flatting stone. The opened cylinder of glass, after passing the heating flues, is pushed forward into the first of the eight compartments of the flatting oven, and passes from there with the entire portion of hearth into the second compartment, under which the firing is

placed, and in which the flatting and smoothing is carried out. From this it passes into the third compartment and so on, until the seventh, from which it is pushed out for further cooling through the passage of communication, into the annealing oven. Under the eighth compartment is placed a second fire, by which the hearth is re-heated for another revolution. The annealing oven is constructed upon the same principle as the flatting oven, except that, instead of lying upon a flatting stone, the sheet of glass there lies upon wires. After one revolution in this oven the sheets of glass are sufficiently cooled to allow of their being taken out. The sheets of glass, as they come from the flatting oven, have a length of from 40 to 50 inches, and a breadth of from 20 to 30 inches; these dimensions, however, are frequently exceeded.

The finer sorts of sheet glass are afterwards polished, as described at p. 329.

Plate Glass.—Formerly plate glass was generally prepared according to the method adopted in the cylinder glass manufacture. Perfectly smooth plates, however, were never obtained in this way; but being like window glass clouded and impure, they consequently gave distorted images. It was not until after Stewart, in the year 1691, introduced the casting of mirrors that perfectly even plates could be prepared. Since that time casting has gradually supplanted the cylinder method for making mirror glass.

The plate-glass furnace usually contains ten or twelve glass pots; they are round or oval, and open above. Besides these pots for melting the glass, square vessels made of clay and called cisterns or cuvettes are used for the melted glass to settle in and become clear. Each cistern is capable of holding as much glass as is required for a single plate; they are therefore of three sizes, small, medium, and large. The cisterns are surrounded by a groove about $1\frac{1}{4}$ inch broad and $2\frac{1}{2}$ inches deep, in order to furnish a hold for the tongs (T, fig. 194) by which they are held and suspended from a crane in casting the plates.

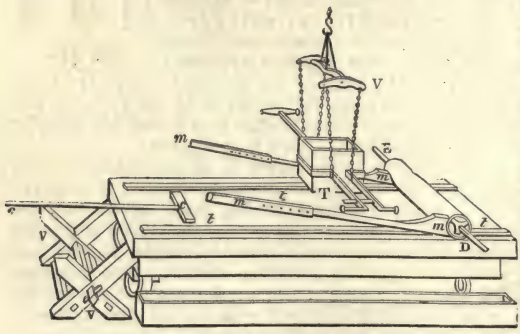


Fig. 194.

The carefully mixed glass materials are put into the glass pots in three successive portions, each addition being made when the former portion has melted. The process of heating is divided into three periods—the fusing, the clearing, and the red heat. If the process of melting does not advance equally in the different pots in a furnace, the progress of those that are behind is hastened by the addition of glass cullet. The fusing period lasts about seven hours and the clearing period about six. After these two periods the fire is moderated and the metal is brought to the proper consistence for casting. The time required for casting 12 plates is about an hour. After the metal has been for some time in a state of fusion, a previously cleaned cistern is placed in the furnace and the opening is closed and plastered up. When the cistern has acquired the temperature of the furnace, the liquid glass is removed by means of a copper ladle from the glass pots into the cistern, care being taken not to disturb the impurities that have settled to the bottom. After every third dip the copper ladle is cooled by dipping it in water, or it would melt.

The furnace being again completely closed, the metal is allowed to settle and become clear in the cistern for several hours. In order to ascertain whether the glass is ready for casting, a sample is withdrawn by dipping the end of a pipe into the molten metal, and judging from the dependent portion, which takes the form of a pear or tear of glass, whether it has the correct consistence and no longer contains any air bubbles. When the right condition is attained the cistern is removed from the furnace and the metal is poured out upon the casting surface, the construction of which is represented by fig. 194. Only occasionally, in the production of very large plates, are two cisterns of metal used for one plate; but then there is a risk that it will be of two different shades.

Whilst the metal is clearing in the cisterns, the casting table and annealing oven are heated. Formerly the casting tables or plates were made of bronze, but recently they have been made of cast iron; usually they have a thickness of about

8 inches. Experiments have been made with casting tables only 2 inches thick; but the result has been to show that they are only useful for casting small plates containing a small quantity of metal. The other dimensions of the casting tables vary very much, according to the size of the glass plate required. In the larger manufactories the casting table is from 16 to 20 feet long and from 10 to 12 feet wide, the weight sometimes exceeding 35 tons. It is evident that the casting surface must be perfectly even. It is supported upon a strong frame, the feet of which are furnished with iron wheels to facilitate the removal of the table to the annealing oven.

The thickness of the plate of glass is regulated by means of bronze or iron bars (*t t*, fig. 194) corresponding in thickness with the plate to be cast and as long as the table. The distance at which they are set apart from each other regulates the diameter of the plate. In order to spread out the metal equally when poured upon the table, a bronze or cast-iron cylinder (ED) is used, 16 to 24 inches thick, weighing from a ton to a ton and a half, and supported by and rolling upon the side bars (*t t*). It is very essential that this cylinder should be perfectly round and free from air holes or other flaws upon its surface. The cylinder is worked by means of two handles which are fixed to its axis.

When the cistern is taken out of the furnace it is placed upon a waggon and wheeled quickly to the casting table; there it is seized by the tongs (T, fig. 194) and suspended to the chain of a crane, by which the cistern is raised, and after being carefully cleaned on every side is swung at a distance of about a foot above the casting table and then tilted so as to pour the metal upon the table. The cylinder being immediately set in motion distributes the metal equally and skims off any surplus glass into a trough of water. The weight of the cylinder is sufficient to carry all surplus glass before it, and there is thus formed between the cylinder, table, and side bars, a perfectly even plate of the thickness of the bars. At the conclusion of the operation the cylinder and bars are removed and the plate of glass is pushed forward into an annealing oven. In the meanwhile another cistern of metal is being prepared for a fresh casting; but in order to avoid overheating the casting table not more than six plates are cast without intermission upon the same table. If a plate of glass be still soft when it is removed into the annealing oven, its surface easily becomes rough, and this has to be removed by the subsequent polishing.

The annealing oven is sufficiently large to hold six plates. It has usually several openings for the introduction of the plates, and a perfectly level sole covered with fine sand. When the plates are put in the oven it should be of a dull red heat. As soon as it is filled with plates the openings are closed up and kept so for several days until the oven has so far cooled that the glass plates can be taken out without danger. Latterly the annealing ovens have been improved so that the cooling is effected in four days, which renders a smaller number necessary.

The plates, when taken from the annealing oven, are rough and opaque, and before they can be used they require to be ground and polished until they appear perfectly smooth and transparent. Previously to this, however, the plates are examined closely; those without flaws are trimmed at the edges with a diamond, whilst those that have flaws are cut so as to yield the largest pieces possible with the least loss.

The grinding of glass was formerly done by hand, but now machinery is used. A large plate is set in plaster of Paris upon a firm bench, and a smaller plate—to be used as a grinding plate—is set in a similar manner on a large stone and made fast in an iron frame. Between the two plates, coarse sand or crushed fire clay and water are placed, each successive quantity of sand or powder being finer than the preceding, and the grinding plate is then set in motion upon the underlying plate. The motion is partly rotatory and partly reciprocating, so that the opposing parts of the plates undergo a continual change. After the operation of grinding with sand is finished, the sand is rinsed off with water and emery is placed between the plates. The plates having been ground perfectly smooth on one side they are reversed, and the other sides are ground in a similar manner.

According to Newton's method, the glass plate to be ground is so fastened by means of a frame upon a rotating round iron plate that the centre of the glass plate lies outside the centre of the iron plate. The iron plate being rotated, the glass plate, which can also revolve in its frame, is set in motion, and a very rapid and complete polishing is effected. In this case also the different powders are used with water.

The polishing of ground, but still dull, glass plates is also carried out by machinery. The polishing machine consists of a flat board, covered on the under side with thick felt. The felt is impregnated with colcothar or ferric oxide. For this purpose the ferric oxide from the Nordhausen acid manufactories is sometimes used after being purified and reduced to a fine powder.

The glass plate is polished until it has a perfectly brilliant surface; it is then re-

moved and washed with very dilute hydrochloric acid, to remove any adhering gypsum or polishing powder.

Optical Glass.—The preparation of glass for optical purposes requires to be conducted with the greatest care in order to obtain the requisite homogeneity and freedom from colour. The furnace used by Bontemps for the purpose is represented, in vertical and horizontal sections, by figs. 195 and 196. A is the bank, with furnaces on each side; B the covered crucible, the mouth of which is opposite the working space; C a stirring iron fastened into a difficultly-fusible clay cylinder (d); f is a trestle carrying a roller upon which the stirrer works to and fro.

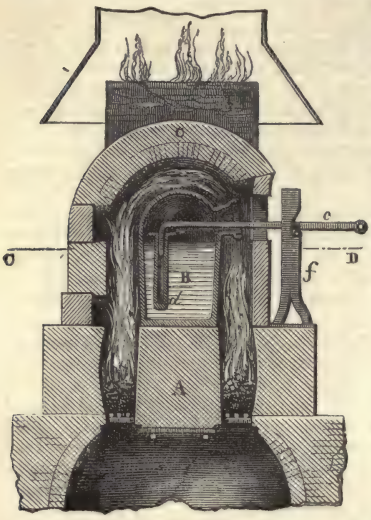


Fig. 195.

The melting pot is first made red hot, then placed in the previously heated melting furnace, and its opening closed with a double lid. The furnace is then brought to the highest possible temperature for three hours, and when the required heat has been obtained the lid is taken from the opening of the melting pot and about 20 lbs. of the

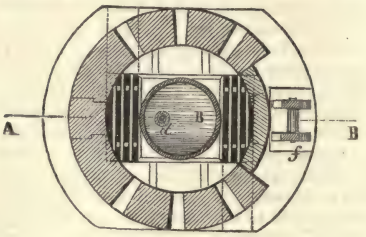


Fig. 196.

flint glass mixture (p. 319) introduced. After an hour a further quantity of 40 lbs. is added; two hours afterwards 80 lbs. more, and this is continued until, in from 8 to 10 hours, the entire charge has been put into the crucible. After 4 hours further heating of the closed crucible, the stirrer, previously brought to a red heat, is introduced, and worked about so as to produce a uniform mixture of the metal and promote the escape of all air bubbles. After 3 minutes the stirrer is taken out, the fire-clay cylinder being left at the side of the pot; the opening of the melting pot is again closed and the fire increased. Five hours afterwards the metal is again stirred, and after that it is stirred every hour. A layer of coal about a foot thick is then put upon the fire, and the temperature being thus somewhat reduced, the crucible is left for the next two hours to allow bubbles to escape. By the end of this time the heat again rises, and it is then got up as high as possible for about 5 hours, until the metal attains its maximum fluidity. The supply of air to the furnace is then checked, and the metal is continually stirred until it thickens and the stirring begins to become difficult. The stirrer and the clay cylinder are then withdrawn, the furnace perfectly closed, and left to cool gradually for about 8 days, after which time the crucible is taken out.

The glass generally forms one mass, which is polished at opposite ends in order to ascertain the portions that are uniform and free from flaws. The pure portions are cut out, and the irregular-shaped pieces—which are cut as large as possible—are then heated in a furnace or under a muffle until they become so soft that they can be pressed into bronze moulds; the finished lenses are afterwards placed in an annealing oven.

The crown glass used for optical purposes (p. 319) is made in the same manner as the flint glass, but as it is less fusible it requires a higher temperature, and is to that extent more difficult to make.

The crucible is placed in the furnace as in the preparation of flint glass, and after being brought to a white heat the mixture is put in so as to complete the charge in 8 hours. After 4 or 5 hours the stirrer is used, and this is done again every 2 hours; the heat is then allowed to go down for 2 hours, afterwards increased as much as possible for 7 hours, the metal again stirred, and after closing the openings of the furnace completely it is allowed to cool gradually. The remainder of the treatment is the same as with flint glass.

ENAMEL.—This name is applied to the vitreous preparations used for coating metallic surfaces, either to protect them from oxidation or for decorative purposes. Enamel is generally rendered opaque by the addition of stannic oxide, and sometimes it is coloured with various other oxides. It is applied to metallic surfaces in the state of powder and is then melted by exposing the articles to a suitable heat in a muffle or kiln.

In the production of ordinary white enamel, crystal glass is thoroughly incorporated with a mixture of zinc oxide and lead oxide by carefully melting them together. The oxides are prepared by mixing an alloy of tin and lead in proportions varying between 15 and 40 parts of tin to 85 and 60 parts of lead in contact with air until it is completely oxidised. The whiter and more opaque the enamel is required to be the larger is the proportion of tin that must be used. As however a large proportion of tin oxide affects the fusibility of the enamel, a smaller amount of sand is used in such case.

The most diverse mixtures are used as the basis of coloured enamels. The principal requisites are that it should be perfectly colourless and more easily fusible than the white enamel upon which it is to be laid. The following are two mixtures used for the purpose :—

	Parts by weight.	
Sand	—	3
Crystal glass	3	—
Calcined borax	1	3
Chalk	—	1
Cubic nitre	¼	—
Antimonic oxide	1	—

The materials used for colouring enamel are in general the same as those already mentioned as being used for colouring glass.

The enamelling of gold articles is effected by making the surface to be enamelled as rough as possible, spreading the enamel upon it, and then heating in a muffle furnace until the enamel melts. The enamel then remains closely adherent to the roughened surface.

In enamelling dial plates the enamel powder is mixed with water and is spread upon both sides of thin sheets of copper, which are then heated in a muffle furface until melted. The figures are afterwards burnt on in black enamel.

The enamelling of kettles, pipes, and other utensils is carried out according to different methods. One consists in first etching the smooth metallic surface of the object to be enamelled with dilute sulphuric acid ; this is washed completely off, and after the article is dried, its surface is smeared with a solution of gum arabic and sprinkled with the enamel powder, and it is heated in a muffle furnace to about 100° or 120°. It is next removed to another muffle furnace and there heated so strongly as to melt the enamel, the operation being watched through a hole in the muffle. Lastly it is slowly cooled in an annealing oven. Should the enamel surface be imperfect the article is again coated and reburnt. The mixture used by Paris consists of :—

Flint glass	130
Sodium carbonate	20·5
Boracic acid	12

These ingredients are carefully melted together in a crucible, the enamel poured out, and after cooling crushed and ground to a fine powder.

According to a second method the iron surface is first covered with a ground coating and then with an outer coating of the actual enamel. The object of the ground coating, which must possess a certain degree of pliability, is to prevent the separation of the actual enamel through unequal expansion caused by heating.

The following are the ingredients for the ground coating, according to Heeren :—

	I.	II.
Quartz powder	30	30
Borax	16·5	25
White lead	3	—
Powdered feldspar	—	30

These ingredients are all brought into as fine a powder as possible, and melted together in a large Hessian crucible placed in a reverberatory furnace. At the bottom of the crucible is a hole, which, until the complete melting of the mixture, is stopped with a plug of quartz powder. As soon as the fusion is accomplished the plug is driven in by an iron implement, and the melted mass run into a vessel placed beneath, and filled with cold water. It thus becomes divided into small pieces and is more

easily ground. To the product obtained from mixture I is added the following mixture Ia, or to mixture II the mixture IIa:—

	Ia.	IIa.
Quartz powder	9	—
Pipe clay	8⅔	10¾
Feldspar	—	6
Magnesia alba	3·5	1¾

The following are two mixtures used for the outer coating, the essential difference between them being that the first contains no lead:—

Quartz powder	37½	37½
Borax	27½	24
Tin oxide	30	25
White lead	—	15
Sodium carbonate	15	11¼
Saltpetre	10	10
Magnesia alba	5	5

The mixture is melted and broken up in the same manner as that for the ground coating, and is then ground to a fine powder with the following addition:—

Quartz powder	6½
Tin oxide	3⅜
Sodium carbonate	⅜
Magnesia alba	¾

In the application of the enamel the articles are first treated with dilute sulphuric acid, and afterwards scoured bright with sand, washed and dried. The powder for the ground coating is then made into a thin paste with water and laid on, dried in a furnace, and afterwards fired in the usual way in a muffle. Upon this basis the outer coat is laid and dried in the same manner.

SOLUBLE GLASS OR WATER GLASS.

This material is an alkaline silicate containing relatively to silica a larger proportion of alkali than ordinary glass.

Composition.—There are two kinds of water glass: potash water glass, which consists of potassium silicate, and soda water glass, consisting of sodium silicate.

Soda water glass contains from 72 to 75 per cent. of silica, and potash water glass from 64 to 69 per cent.

Characters.—Water glass when pure is colourless and transparent, but is more generally of a yellowish or brown colour, which is due to impurities. It is soluble in water, and the solution when evaporated leaves the silicate in the form of a glassy film upon the surface to which it has been applied.

Preparation.—Fuchs recommended for the preparation of water glass the following proportions of ingredients, which are melted together in a crucible:

	Potash water glass	Soda water glass	
Quartz	45	45	100
Potash	30	—	—
Calcined soda	—	23	—
Sodium sulphate	—	—	60
Wood charcoal	3	3	20

On exposing the melted mass for a short time to the action of the air, the salts that have not been converted into silicate effloresce and may be washed away. When required for use water glass is dissolved in hot water.

Schür gives the following recipe for preparing water glass:

	Soda water glass	Potash water glass
White sand (containing 90 per cent. SiO_2)	180	180
White Jarrow soda (52 per cent.)	100	—
Ordinary potash (90 per cent.)	—	125
Powdered wood charcoal	3	3

Water glass may also be prepared in the wet way, by dissolving siliceous infusorial earth in a boiling solution of caustic soda, having a specific gravity of 1·15. In order

to separate from the solution organic substance derived from the infusorial earth, a small quantity of lime water should be added to it. The solution is then allowed to settle, is afterwards decanted, the clear liquid evaporated to a syrupy consistency, and the solid residue dried in the air.

Kuhlman prepares water glass by heating together caustic soda, or potash and broken flints, in a suitable digester, under a pressure of 7 atmospheres, until the liquid is saturated with silica.

Uses.—Water glass is used for painting over plastered walls, both in the interior and exterior of buildings. Three coats are generally given.

For this purpose pigments are often mixed with the water glass, such as chalk, ochre, green earth, etc. A light blue colour is given by the addition of ultramarine and chalk or heavy spar. By penetrating into the porous surface of the plaster, and drying in it, or perhaps combining chemically with the lime, the water glass gives a shiny appearance to the surface, which not only serves to keep it clean, but admits of its being washed even with soap and water. In choosing pigments for mixing with water glass, care must be taken to avoid using any that would cause decomposition, like zinc white, white lead, chrome yellow, Prussian blue, mineral blues, Schweinfurt green, etc.

Water glass is also used for painting over limestone that is liable to disintegrate. Chalk as well as porous limestone is rendered very hard and weather proof by water glass, and the surface becomes smooth, but at the same time of an undesirable yellow colour.

For coating wood, the solution of water glass should be applied only as a thin solution in quantity sufficient to penetrate the wood; otherwise it is very liable to peel off, owing to the slight adhesion between wood and water glass. Wood thus treated with water glass becomes darker in colour; it does not ignite readily when exposed to the action of flame, although, when thrown into a fire, the inner portion becomes entirely carbonised.

Water glass adheres very readily to iron and other metals, protecting them from rust, and even from oxidation at a high temperature, on which account it is useful for painting iron stoves and stove pipes. When mixed with pigments, it is also used for painting glass.

Water glass is useful for cementing glass, porcelain, and similar substances. For this purpose the pieces to be united are heated up to the temperature of boiling water, the edges of the pieces to be united are then moistened with a hot concentrated solution of water glass, pressed together, and bound round with string. When the water glass has thoroughly dried, which in the case of small objects takes a few days, and with pieces about an inch thick about fourteen days, the cement attains such hardness that the objects repaired may be used as before.

In calico printing water glass is used for fixing ultramarine.

POTTERY OR EARTHENWARE; PORCELAIN, ETC.

The art of making vessels of clay is one of the most ancient branches of industry, and although very great improvements have been made at various times in matters of detail, the manufacture of earthenware is still conducted essentially in the same manner that it was originally. The fundamental facts upon which this manufacture is based are to be found in two of the characters of the aluminous silicate which occurs naturally as clay, viz., the hardening it undergoes when heated to a sufficiently high temperature and the plasticity it possesses when mixed with water. In these and other respects the various kinds of clay differ very considerably on account of differences in their chemical composition, and consequently it is necessary to make suitable allowance for such differences, either by modifying certain operations or by adding to the clay other materials; but in all cases the manufacture of earthenware consists in preparing an argillaceous dough or paste of such a consistence that it can be wrought into, and retain the various shapes required, and then subjecting the articles made from it to such a degree of heat as will give them the desired hardness and coherence. In all cases the selection of a suitable description of clay is a most important point, both as regards the nature of the articles to be made, and the particular treatment to be adopted in the manufacture.

The purer varieties of clay, consisting almost entirely of aluminum silicate, are either white or of a slight greyish tint, and they are extremely refractory even at the highest temperatures. Many varieties of clay, however, contain besides aluminum silicate other silicates or oxides, etc., which make the clay more susceptible to the influence of heat, and sometimes even fusible, while at the same time these substances

often communicate colour to the clay. The commoner kinds are generally of a brown, red, or yellow colour. The composition varies considerably, as shown by the following table.

	Common Clay	Poole Clay	Sandy Clay	Yellow Clay	Pipe Clay	Fire Clay	Fuller's Earth	China Clay	
Locality .	—	—	—	—	—	—	—	Cornwall	Halle
Analyst .	—	Weston	—	Brown	—	Tookey	—	—	—
Silica . .	49·44	48·99	66·68	58·07	53·66	65·10	53·10	46·32	39·62
Alumina .	34·26	32·11	26·08	27·38	32·00	22·22	10·00	39·74	45·00
Lime . .	1·48	0·43	0·84	0·50	0·40	0·14	0·50	0·36	0·07
Magnesia .	5·14	0·22	trace	trace	trace	0·18	1·25	0·44	3·32
Ferric oxide .	7·74	—	—	—	—	—	9·75	—	—
Ferrous ,, .	—	2·34	1·26	3·30	1·35	1·92	—	0·27	—
Alkaline bases	—	3·31	—	—	—	·18	trace	12·67	—
Water . .	1·94	11·96	5·14	10·30	12·08	9·28	24·		10·00
	100·	99·36	100·	99·55	99·49	99·02	98·60	—	—

The effect of heat upon clay differs according to the amount of lime and ferric oxide or ferrous oxide it contains; those kinds containing but very little of these substances are known as fire clay, on account of their capability of bearing very high degrees of heat without melting, and they are used for making crucibles, glass pots, and the bricks for building furnaces, etc. Iron is a frequent constituent of clay, either in the state of silicate or as oxides, and it is to one or other of these substances that the red, blue, or yellow colours of many kinds of clay is due. When clay of this kind is subjected to action of heat, and especially when it is brought into contact with carbonaceous vapour from the fuel used, there is a possibility of its melting in consequence of the formation of a comparatively fusible ferrous silicate. The presence of lime as silicate or carbonate has a similar influence, though in a less degree. Clay containing so much iron as the Fuller's earth in the above table would be too readily fusible to use for pottery ware, and even when the amount is less care must be taken in firing the articles made with such clay that the temperature is not raised too high. For this reason it is only the purer kinds of clay, such as that occurring at Poole and other parts of Dorsetshire and Devonshire, that are suitable for the manufacture of the better kinds of earthenware, while in the manufacture of porcelain only the finest kind of clay, known as kaolin or china clay, can be used.

Clay frequently contains calcium carbonate or magnesium carbonate, and is then termed marl, which is distinguished as aluminous or calcareous, according as the clay or the carbonate preponderates. These materials are often used in the manufacture of earthenware, bricks, etc. The mixture of clay with sand, gravel, etc., which frequently occurs in the more recent geological formations, and is known by the name of loam, is used chiefly for brick-making.

The colour of clay as it occurs naturally is sometimes due wholly or in part to the presence of organic substances, and in such cases the clay frequently burns white, unless it contains iron in addition.

When clay consisting only of pure aluminum silicate is, in technical language, burnt, or exposed to the influence of a temperature sufficiently high to give it the maximum degree of coherence; it contracts and the mass becomes much denser. Since this shrinking of clay in burning would have the effect of distorting vessels made of it or causing them to crack when fired, it is necessary to counteract the contraction of the clay by mixing with it a sufficient proportion of some other material which is not susceptible of contraction when intensely heated. Silica is the substance used for this purpose either in the state of sand for the coarser descriptions of clay ware, or for the better kinds of ware as finely divided flint or quartz. The clay used in the manufacture of porcelain, and known by the name of china clay, generally contains, besides aluminum silicate, a considerable amount of finely divided silica. In order to prevent the shrinking it is also customary in preparing the clay for moulding to mix with it a quantity of broken fragments of the same kind of ware that is to be made or some previously burnt clay, etc.

Although, by the operation of burning, clay is rendered permanently coherent, and its texture is thus so far altered that it is no longer susceptible of disintegration or becoming soft when in contact with water, it is still so porous that it is capable of

absorbing water or other liquids, and even allows liquids to percolate through its mass. For many of the purposes to which vessels of clay ware are applied this character would be very objectionable; consequently, it is necessary to render the surfaces of the articles impermeable, and this is done by coating them with a thin layer of siliceous material that is much more readily fusible than the clay of which the ware is made. This coating is generally applied after the ware has been partially burnt, and when it is fired again the fusible coating melts, forming upon the surface of the articles a smooth vitreous film called the glaze.

Another method of rendering earthenware articles impervious is to mix intimately with the clay another substance which is much more fusible, and at the temperature to which the ware is exposed in firing it, this admixture becomes sufficiently soft to permeate the particles of clay, so as to cement them together and render the mass semi-vitreous or even translucent in the case of the finer kinds of ware, such as porcelain.

Pottery ware presents very great differences of character according to the nature of the raw material used in the manufacture and the treatment to which it has been submitted, and while the difference between some kinds is considerable, it is in other cases so slight that no essential distinction can be recognised. There is, however, one feature in regard to which all varieties of pottery ware may be distinguished as belonging to one or other of two classes.

1. Those kinds of ware in which the texture of the body is similar to that of burnt clay, and, independently of the glaze by which the surface is rendered impervious, the body remains porous after burning. This class comprises the commoner kinds of earthenware or terra cotta, common roofing tiles, bricks, etc.

2. Those kinds of ware in which the texture of the body is throughout stony or partially vitreous, in consequence of the more intimate aggregation of its particles by the softening of the mass during the burning. This class comprises, besides porcelain, several of the finer kinds of earthenware nominally distinguished as stone china, Wedgwood ware, stoneware, etc., and some of the better kinds of bricks, tiles, etc. present characters of a similar nature.

Under the general name of earthenware several varieties of pottery are comprised, in all of which the body has an earthy texture and is porous and opaque. Delft and majolica wares are of this kind. In the finer kinds of earthenware the body is denser and harder, besides being to some extent vitrified. The best kind is called iron stone china, and the wares belonging to this class present almost innumerable differences of degree. The fine stoneware commonly called Wedgwood is a still closer approximation to porcelain, and common stoneware is of the same character essentially, but is made of coarser material and is less carefully prepared.

The following table of analyses of different kinds of pottery ware will serve to show the differences that exist between them in regard to composition:

	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Calcium phosphate	CO_2	Alkali
Earthenware, Delft	49·07	16·19	18·01	0·82	2·82	—	13·09	—
„ Majolica	48·00	17·50	20·12	1·17	3·75	—	9·46	—
„ Italian	49·65	15·50	22·40	0·17	3·70	—	8·58	—
„ Spanish	46·04	18·45	17·64	0·87	3·04	—	13·96	—
„ French Paris	61·50	12·99	16·24	0·15	3·01	—	6·10	—
„ French Rouen	47·96	15·02	20·24	0·44	4·07	—	12·27	—
„ French Nevers.	56·49	19·22	14·96	0·71	2·12	—	6·50	—
Common English ware	68·55	29·13	1·24	—	—	—	—	—
Chinese porcelain, inferior	68·96	29·24	1·60	—	—	—	—	—
„ „ superior	71·04	22·46	3·82	—	—	—	—	2·68
Berlin „	72·96	24·78	1·04	trace	—	—	—	1·22
English „ No. 1	39·88	21·48	10·06	—	—	26·44	—	2·14
„ „ No. 2	40·60	24·15	14·22	0·43	—	15·32	—	5·28
„ „ No. 3	39·68	24·65	14·18	0·31	—	15·39	—	5·79
Stoneware Vauxhall	74·00	27·04	0·60	0·17	2·00	—	—	1·06
„ Frechen	64·01	24·50	0·56	0·92	8·50	—	—	1·42
„ Wedgwood	66·49	26·00	1·04	0·15	6·12	—	—	0·20

The analyses at the top of the table show that the several kinds of ware which they represent are essentially different from true porcelain, such as that of China or Germany; and the presence of undecomposed carbonate shows that they were fired at a moderate heat. Ordinary English earthenware is intermediate between this kind of ware and true porcelain, and this differs from stoneware chiefly by reason of the

purity of the material it is made from. English porcelain is peculiar in containing calcium phosphate as an essential constituent.

Common Pottery Ware.—The clay used for making articles of this description is carefully selected and prepared, chiefly by mechanical means, in such a manner as to have a very uniform texture and considerable plasticity. The shaping of the articles is performed upon the potter's lathe, the construction of which is represented by fig. 197.

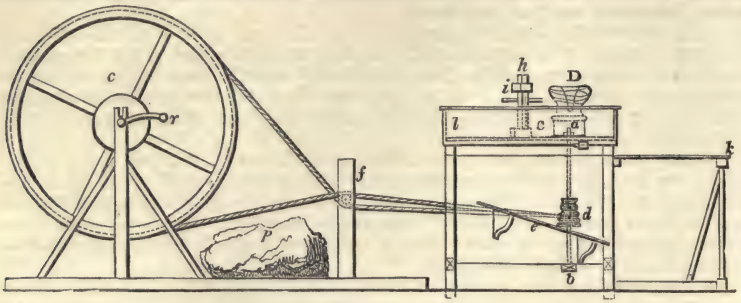


Fig. 197.

It consists of an upright shaft *a b*, the lower end of which runs in a step fixed to the frame of the table (c), through which the head of the shaft projects into a block (*a*) called the head of the lathe. The upright shaft is fitted with a pulley (*d*) having several grooves for receiving the driving cord passing over the guide pulley (*f*) and the wheel (*e*), to which motion is communicated by the winch (*r*) and the head of the lathe (*a*) is thus made to revolve rapidly. The workman sits upon the bench (*k*) and placing a lump of prepared clay upon the head of the lathe while it is revolving, moulds it with his hands into the desired form. This operation is termed throwing. In large works the lathes used for shaping clayware are of improved construction, and are often driven by steam power; but in principle they do not essentially differ from the most primitive form of potter's wheel represented above, which has been in use from the remotest period. After the vessels have been moulded, they are thoroughly dried in covered sheds to which the air has free access, and sometimes the sheds are warmed by flues under the floor.

On account of the fusibility of the clay used in making the coarser kinds of pottery they are burnt at a comparatively low temperature. The kilns used for the firing are often very rudely constructed brick chambers heated by a fire at the side; sometimes long horizontal reverberatory furnaces are used, the construction of which is represented by fig. 198. The chamber (A) in which the articles to be burnt are

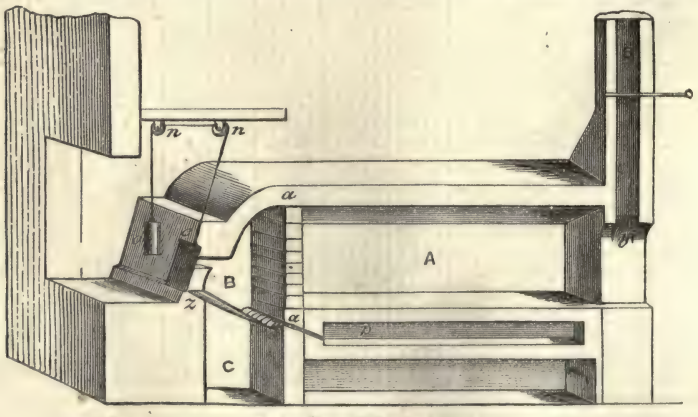


Fig. 198.

placed is heated by the hot gas passing from the fireplace (B) through the perforated wall (*a a*) which separates the fire from this chamber. The fire grate slopes from the furnace door (*z*) down towards the kiln to facilitate the firing and stoking, and

the door can be raised by means of the weight (*o*) attached to a chain passing over the pulleys (*n n*). The chimney is furnished with a damper (D) for the purpose of regulating the draught. The hollow space (*p*) beneath the firing chamber serves to keep the brickwork dry, and at the side of the chamber there are several smaller flues for the same purpose. The firing chamber is charged and emptied through the archway (*b*), which is bricked up when the kiln is in use.

In many instances common pottery is used without being glazed. When it is required to be impervious the glaze is produced either by dusting the moulded articles while moist with a finely powdered material consisting of clay, sand, and litharge in such proportions as to form a very fusible lead and alumina silicate when the ware is fired. A coloured glaze is produced by adding to the mixture various metallic oxides. The glaze applied to such ware as is known by the terms fayence, majolica, delft, etc., is often more of the nature of enamel, and is made opaque to conceal the dark colour of the body. Stannic oxide is used for this purpose in preparing the glazing material, together with some lead oxide to give the requisite fusibility. The two metals are generally alloyed together in the proportion of three parts lead to one of tin, and then converted by roasting into the state of oxide, which is mixed with various proportions of sand, soda ash, or common salt, and sometimes the decomposed felspar known as Cornish stone, and the mixture is heated in a reverberatory furnace until it begins to melt and becomes pasty or fritted, as it is termed. The agglutinated material is then thrown into water and finely ground to make it fit for applying to the ware.

Sometimes the glazing material is made into a paste with water and is applied to the surface of the moulded vessels in that condition, or it is mixed with sufficient water to form a thin sludge into which the partially fired articles, termed biscuit ware, are dipped. This latter plan of applying the glazing material is the best, but it is also the most expensive, since it involves the necessity of firing the ware twice, and is therefore seldom adopted, except in making superior kinds of earthenware.

The better varieties of glazed pottery with a porous body, which are somewhat vaguely termed earthenware, are generally made either with a mixture of clay, marl and sand, or with a paste composed of plastic clay and powdered quartz or flint. In the former case the ware when fired is soft, and contains so much undecomposed earthy carbonate that it effervesces with acids; in the latter case the ware is much harder and more compact. The temperature requisite for firing the body of fine earthenware is higher than that requisite for common ware, and it is much higher than the glaze will bear; consequently articles of this kind are always fired twice, in the first instance to render the body sufficiently hard and compact, and afterwards, when the glazing material has been applied, sufficiently to melt the glaze uniformly over the entire surface of the articles. In firing these kinds of earthenware the articles are never exposed to the direct action of the flame, but are enclosed in cylindrical envelopes called saggers, made of refractory material, and these are piled up one upon the other in the kiln. Slabs of clay are sometimes used instead of saggers for common wares, and they are arranged round the articles to be fired so as to protect them from contact with the flame. The articles require also to be separated from each other by means of triangular bars of hard burnt clay, so as to prevent them from sticking together in consequence of softening. This precaution is necessary even in the first firing in the biscuit kiln, and it is still more so in the second firing when the glaze is burnt on. The material used for producing the glaze is a mixture of felspar or Cornish stone with alkalies, borax and lead oxides. The glaze is either colourless and transparent, or when the body of the ware is dark coloured, it is made opaque by the addition of stannic oxide, and is sometimes coloured with other metallic oxides.

The decoration of the ordinary varieties of earthenware is generally effected by transferring to the surface of the biscuit ware an impression of the intended design that has been printed upon thin paper, with ink composed of suitable pigments and linseed oil varnish. The paper is then washed off, leaving the design attached to the surface of the ware, and it is burnt in by a special firing operation. The chemical characters of the pigments used for this purpose must be such that they will resist not only the influence of heat in burning them in, but also that of the glaze material which is generally applied to the ware afterwards. For blue, cobalt oxide is used, and various shades are produced by mixing with it zinc oxide; for green, chromous oxide or cupric oxide is used; for yellow, uranium oxide, lead chromate, ferric oxide, or potassium antimonate; for red, cuprous oxide or ferric oxide; for violet and rose-colour, purple of cassius; for pink, chromium stannate and calcium stannate. Sometimes the designs are printed upon the glaze after coating it with a layer of varnish.

Ordinary earthenware is not often decorated otherwise than by printing, and it is only the superior kinds that have designs painted by hand in the manner that fine pottery ware like porcelain is ornamented. Brilliant metallic films called lustres are sometimes produced on the surface of ordinary earthenware by applying dilute

solutions of metallic salts and afterwards exposing the articles to the reducing action of hot air containing smoke, which has the effect of reducing the metal.

The kiln used for firing this kind of pottery is represented by figs. 199, 200, 201, 202. The body of the kiln is a cylindrical domed chamber (D), the interior of which

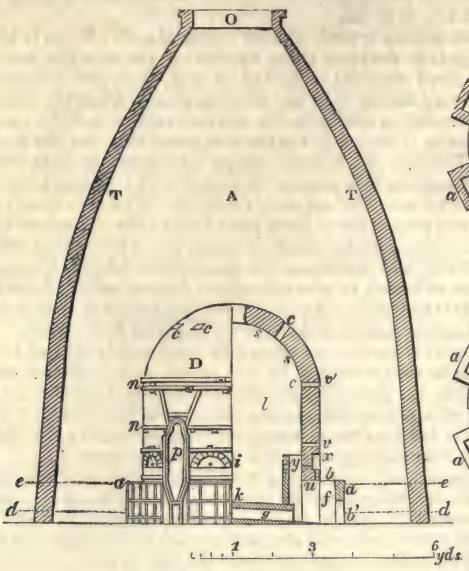


Fig. 199.

Fig. 200.

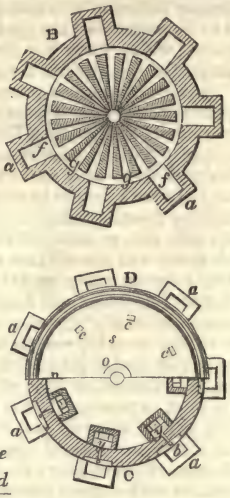


Fig. 201.

(*l*) communicates with the fireplaces (*f*) of the furnaces (*a a*) by the vertical and horizontal flues (*y g*), shown on a larger scale in fig. 202. The kiln is surrounded by a conical tower (T T) called the howell, into which the hot gas escapes from the kiln through the small apertures (*c c c*) in the dome and is discharged from the throat (O) or lunette of the howell. Fig. 200 is a horizontal plan of the kiln (at the line *d d*), showing the arrangement of the radiating and circular horizontal flues (*g*, fig. 199) and the fireplaces (*f*). Fig. 201 represents on one side (c) a plan of the kiln at the line (*e e*), showing the disposition of the fireplaces (*f*), the upper mouths (*b*) of the furnaces, as well as the vertical flues (*y*), and the horizontal peep-holes or registers (*x*) which pass into the vertical flues, and are also shown on a larger scale in the vertical section of one of the furnaces (fig. 202). The other half (D) of fig. 201 is a bird's-eye view of the top of the kiln dome (*s*) and the disposition of the vent holes (*c c*). The register slits (*v*) and (*v'*), fig. 199, are for regulating the heat in the kiln and the door (*p*) is for charging and emptying the kiln. The draught passes in a downward direction through the upper mouths of the furnace (*b*), and the flame is divided into two parts on entering the kiln, one part passing horizontally into the flues (*g*), under the sole (*k*) of the kiln, and converging towards the centre, enters the interior of the kiln at that point, while the other part passes up through the low flues or bags (*y*) into the body of the kiln.

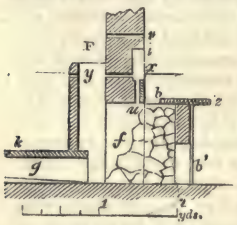


Fig. 202.

The saggers containing the articles to be burnt are piled up in the space between the furnaces in such a way that the top of one sagger is closed by the bottom of the one above it, and they are built up in stacks until the kiln is full. The door (*p*) of the kiln is then bricked up, the fires lighted, and the heat maintained for two or three days at a proper degree. During the firing the lower furnace mouths (*b'*) are kept closed, fuel is supplied through the upper furnace mouth (*b*), and the heat is regulated by the tiles (*z*). By means of small cups made of the same clay as the ware that is being burnt, which are taken out and examined at intervals, the progress of the operation is judged of, and when it is completed the kiln is allowed to cool very slowly until the temperature has fallen low enough to take out the saggers. As the

biscuit ware is taken out of the saggers, it is dipped into the glazing material, dried, and then submitted to a second firing in the glaze kiln.

Porcelain.—The materials used in the manufacture of this kind of clayware are chiefly the white clay called kaolin, quartz, or some other kind of pure silica, and felspar. These materials are very intimately mixed in such a manner that, while the infusible kaolin gives plasticity to the mass that admits of its being shaped, the other ingredients constitute a fusible mixture or flux which undergoes partial fusion, when the ware is exposed to a high temperature, and thus forms a kind of cement by which the particles of kaolin are permeated and held together. The mass consequently acquires a considerable degree of translucency which is characteristic of this ware.

The preparation of the materials involves a number of operations, chiefly of a mechanical nature, having for their object the production of extreme uniformity in the paste or mass of which porcelain articles are made. The clay is in the first instance worked with water to separate undecomposed felspar and sand, then submitted to a process of elutriation so as to obtain it in a state of very minute subdivision. The felspar and other ingredients, such as gypsum, chalk, and fragments of broken porcelain, are ground to an equally fine powder in mills having the construction represented by fig. 203.

These mills consist of two stones (B B′), the lower one being fixed upon a solid bed (*b*), while the upper one can be made to revolve by the shaft (M″), and gearing (M M). Both stones are enclosed in a vat (C) hooped with iron. The siliceous or felspathic materials are ground in these mills with water, and when reduced to a state of sufficiently fine subdivision the sludge is run out through the spigot hole (*c*′).

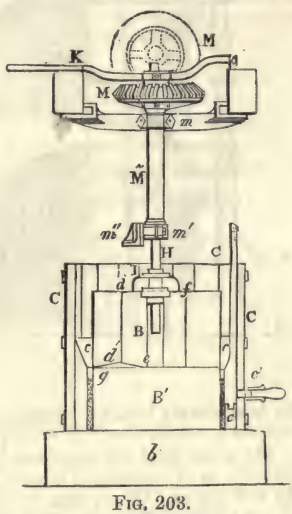


Fig. 203.

The vat (C) extends above the upper moveable millstone (B), and the lower stone (B′) is surrounded with a strong wooden ring which is funnel-shaped at the top (*c*) in order to throw back any fragments forced upwards by the motion of the stone. The millstone (B) is not perfectly round, but has a portion cut away on two sides so as to guide the materials under the grinding surface, which is also grooved, as shown at *d e g*, in order that the materials being ground may be retained between the surfaces of the stones.

When the grinding of the siliceous or felspathic material is nearly completed, the mass aggregates together at the bottom of the vat as a tenacious pasty magma, and when the mill is not kept running at sufficient speed it is liable to be set fast.

In mixing the ingredients, great care is required to secure the proper proportions; and as this is an essential condition of the production of a suitable paste, regard must be had to the composition of the raw materials used. At the porcelain works at Sèvres it is usual to make the paste so that it has the following composition percentage:

Silica	Alumina	Potash	Lime
58·0	34·5	3	4·5

The finely divided materials are mixed by long-continued stirring in the state of thick sludge in large wooden vats, and the excess of water is then removed, either by drawing off the mud into boxes fitted with plates of plaster of Paris at the bottoms which absorb the water or by pressure in bags. When the mass is thus reduced to a pasty consistence, it is kneaded and worked together into lumps by the hands and feet of workmen until it becomes sufficiently plastic. The lumps of paste are then placed in layers in a moist place, and left for some length of time, to undergo a process termed mouldering, in the course of which the paste acquires a dark grey colour, and evolves sulphuretted hydrogen, while at the same time it becomes more plastic.

Porcelain articles are either shaped upon a potter's wheel or by pressing sheets of the paste between moulds made of gypsum, and sufficiently porous to absorb water from the paste while it is being moulded, and render it so stiff that it can be removed without bending.

Plaster moulds are also used for casting some articles by pouring into them a liquid mixture of the paste with water. By the absorption of the water into the mould, the paste forms a crust upon the surface of the mould, and when this is thick enough, the superfluous liquid is poured out.

The articles moulded by any one of these methods are afterwards submitted to several further operations to finish them; and then they are thoroughly dried in the air and fired in saggers in the porcelain kiln, which is constructed as shown by fig. 204. It has three compartments (L L′ L″) in which different degrees of heat are produced; the upper compartment serves for drying saggers or baking biscuit ware, while the two lower compartments are used for the subsequent firing of the finished ware. The kiln is heated by four furnaces (A A) arranged round the kiln, and the fuel is thrown in through the mouths (*b′b′*) so as to fill the space (*f*). The draught passes downwards through the mouth (*b′*) of the furnace and the flame enters the kiln through the flue (*p*), which is divided by a kind of grating to disperse the flame in the chamber (L). The ash pit (*b*) is kept closed as well as the small aperture (*o*). The arches (D E) serve for placing the articles to be burnt in the several compartments and removing them when burnt. The draught is produced by an opening (C) at the top of the kiln, the flame and hot gas passing upwards through apertures (*t t t*) in the arch of each compartment.

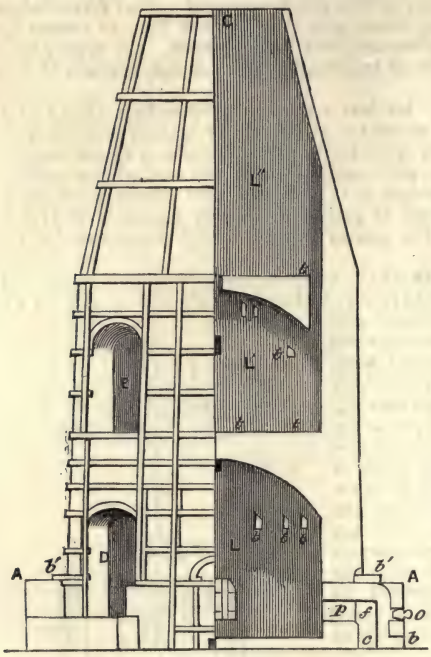


Fig. 204.

Since a very intense heat is required for firing porcelain, the kiln is massively built of refractory bricks, and strongly bound with iron hoops. Such kilns are generally about 20 feet in diameter.

The glaze used for porcelain is a mixture either of kaolin, gypsum, and broken porcelain, or of quartz and felspar very finely ground and made into a thin sludge or slip with water. On dipping the biscuit ware into this mixture, a sufficient quantity adheres to the surface, and after drying the articles they are again fired at a higher temperature than in the first instance.

Another kind of ware, called tender porcelain, is made of a mixture of pure plastic clay, kaolin, Cornish stone or partially decomposed granite, burnt bones, and flint. These ingredients are ground and made with water into a homogeneous paste, which is moulded on the potter's wheel, yielding, when fired, a highly vitrified porcelain. The glaze consists of a mixture of felspathic stone, chalk, soda, and borax.

A kind of semi-porcelain, known by the name of fine stoneware, is extensively made in England from plastic clay mixed with a felspathic material, which acts as a flux, and gives the ware a close texture as a result of partial fusion in the firing. In glazing this kind of ware the interior of the sagger is smeared with a mixture of sodium chloride, potash, and lead oxide, which is vaporised during the firing sufficiently to coat the articles and produce a glaze. The characters of stoneware depend very much upon the quality of the clay used in making it, and there are several varieties of it. The commoner kind, such as jars and bottles are made of, is glazed by exposing it while in the kiln to the action of sodium chloride vapour, which penetrates the substance of the ware, and acts upon the siliceous material so as to form a fusible alkaline silicate. This operation is called salt glazing.

Bricks.—The ordinary bricks used for building purposes are made of common plastic clay, mixed with sufficient sand to produce a mass that will dry without crack-

ing, and bear firing without too much contraction. The temperature at which bricks are burnt must be regulated according to the composition of the clay employed, so as to avoid the melting of the bricks, which might readily occur when the clay contains much iron.

Both loam and marl frequently occur of such a character as to be applicable at once to making bricks, but clay generally requires to be mixed with a certain proportion of sand, and sometimes chalk has to be added when the material used is too sandy. In all cases, it is especially important to render the earth used for making bricks as homogeneous as possible, to make it uniform in consistence, and to separate from it any stones, shells, or remains of plants. This is effected either by kneading the brick earth, or by passing it through a pug mill. To facilitate this operation, the clay is generally exposed to the influence of frost, which causes its disintegration, and sometimes it is mixed with sufficient water to form a sludge, which is run through sieves to separate the coarser particles, and then left to settle in pits until the water can be drawn off. Cinders are often mixed with brick earth for the purpose of preventing the bricks from contracting too much when burnt, and in the neighbourhood of London the siftings of dust heaps are used for this purpose under the name of **breeze**.

The operation of moulding is performed either by hand or by machinery, and the bricks are then piled up in contact with the air, so that they may dry sufficiently to be fired either in kilns, or in clamps constructed of alternate layers of green bricks and breeze, with flues running throughout in communication with the fireplaces, so that, by the combustion of the fuel thus distributed, the entire pile can be heated to a sufficiently high temperature.

The characters of bricks depend upon the composition of the earth from which they are made. When the amount of ferric oxide is considerable, the bricks often have a dark red colour after burning; but in some cases a portion of the oxide is reduced, and by combining with silica, produces a fusible ferrous silicate which has a dark colour and forms a vitreous glaze upon the surface of the bricks. When the brick earth contains little or no iron, the bricks are white or pale coloured.

Tiles for roofing and drain pipes are made of clay mixed with a smaller proportion of sand than is used in making bricks.

Artificial Stone.—Calcium salts and alkaline silicates react upon each other in the presence of water, giving rise to alkaline carbonate and calcium silicate which is a substance of sufficient durability to serve for building purposes. A method of preparing artificial stone in this manner was introduced some years ago by Mr. Ransome. In the first instance he made this stone chiefly of sand, which was kneaded into a firm dough with water glass, and, after being moulded into the shape required, was then saturated with a solution of calcium chloride so as to convert the alkaline silicate in the mass into calcium silicate, which acted the part of a cement and bound the grains of sand into a solid coherent mass that was not susceptible of being disintegrated or acted upon by water.

After the blocks had been submitted to the action of the calcium chloride solution they were washed with water to extract the sodium chloride resulting from the decomposition that had taken place between the alkaline silicate and the calcium chloride, and then were finally baked in a kiln. It was found, however, that the complete removal of the salt was difficult, and that the blocks of stone could not well be acted upon throughout unless hydraulic power was applied for forcing the solution into the mass of sand and alkaline silicate.

An improved application of this idea of making artificial stone consists in using, instead of sand, calcareous materials and silica in the soluble condition for preparing the paste with soluble alkaline silicate. A mixture of limestone, soluble silica, and caustic lime made into a paste with alkaline silicate soon becomes hard, in consequence of the formation of calcium silicate by the action of the lime upon the alkaline silicate. If requisite, it can be still further hardened by treatment with a solution of calcium chloride.

MAGNESIUM.

Symbol Mg. Atomic Weight 24.

History.—This metal was first isolated by Davy in 1808. The distinction between its compounds and those of calcium was not recognised until the middle of the eighteenth century, when Black pointed out the characters which distinguish magnesia from lime. Bergman subsequently gave a more complete description of the chemical characters of the magnesium compounds.

Occurrence.—Magnesium occurs very abundantly in several states of combination, especially in the form of carbonate as magnesite, and combined with calcium carbonate as dolomite; in the state of hydrate it occurs as hydrophyllite, the oxide as periclas, the sulphate as bittersalt, the borate as boracite, the arsenate as a variety of pharmacolite, the phosphate in combination with magnesium fluoride as wagnerite. The silicates occur as a great variety of minerals, such as talc, steatite, meerschaum, serpentine, etc.; also in combination with other silicates, as in hornblende, augite, etc. The chloride and sulphate occur in sea water and many kinds of mineral water. Magnesium also occurs in plant and animal organisms, chiefly in the forms of carbonate and phosphate, or in combination with organic acids.

Characters.—Magnesium is a bluish-white dull-looking metal, moderately hard and malleable, but having very little ductility; its specific gravity is 1·750, it melts at a moderate red heat, and volatilises at about the same temperature as zinc. In a dry atmosphere it does not oxidise, but in contact with moist air it soon becomes covered with a film of magnesium hydrate; when heated to redness in atmospheric air or in oxygen gas it takes fire and burns with a very intense light; it decomposes water slowly, but is rapidly dissolved by dilute acids.

Preparation.—Magnesium is prepared on a large scale by melting in an iron crucible a mixture of magnesium chloride, sodium chloride, and calcium fluoride, with sufficient sodium to separate the metal from the magnesium chloride. The reduced metal sinks to the bottom of the crucible and is protected from oxidation by the layer of melted salt above it. The magnesium is thus obtained free from nitrogen; but as it contains impurities and is too brittle to be worked, it is distilled from a close iron vessel furnished with a discharge tube, by which the vapour is made to pass from the top of the vessel downwards into another closed iron vessel placed underneath, where it is condensed into blocks which are washed and broken up into small pieces. To convert the metal into wire the pieces are packed into a cylinder with a perforated bottom, and when made just hot enough to render the metal soft, pressure is applied by means of the ram of an hydraulic press placed in the cylinder, until the metal oozes out through the perforations in the bottom of the cylinder in the form of wire. By passing the wire through warmed rollers it is converted into a flat ribbon, in which form it is generally used.

Uses.—Magnesium is used for burning, as a source of light for producing photographs, for which purpose it is well adapted, since the light evolved is rich in the rays exercising chemical action; it is also used in preparing fireworks.

Compounds.—Magnesium is divalent and its compounds present considerable analogy to those of zinc; it combines directly with chlorine, bromine, iodine, sulphur, and nitrogen, forming compounds which are represented by the formulæ $MgCl_2$, $MgBr_2$, MgS and Mg_3N_2.

The oxide MgO, known as magnesia, is the only known compound of magnesium and oxygen. It is formed when the metal burns in atmospheric air or oxygen, as a finely divided powder diffused through the remaining gas as a dense smoke. As ordinarily obtained by heating the carbonate to redness, it is a bulky white powder which bears a very high temperature without melting. Its specific gravity is from 3·070 to 3·200, and by strong ignition it is increased to 3·610. Magnesia has neither smell nor taste; it is but very slightly soluble in water, and has an alkaline reaction

upon test paper, but is not caustic. Magnesia is a strong base which combines with acid oxides, forming salts.

Magnesium hydrate, MgH_2O_2, is a white pulverulent substance formed on adding solution of potash, soda or baryta to the solution of a magnesium salt. It occurs naturally as brucite in rhombohedral crystals. Magnesium carbonate, $MgCO_3$, is very sparingly soluble in water; it occurs naturally as magnesite, and can be prepared by heating magnesium sulphate and sodium carbonate to 160°C. under pressure. It combines readily with carbonic acid, forming a solution which has a bitter taste and alkaline reaction; but the acid carbonate, $MgH_2 2CO_3$, has not been obtained in a solid state. It also combines with other carbonates, forming double salts, and on this account ammonium carbonate does not produce a precipitate in solution of magnesium salts. The precipitate produced by fixed alkaline carbonates is a compound or mixture of carbonate and hydrate. Magnesium chloride, $MgCl_2$, is a white translucent substance which melts at a red heat, but is decomposed when heated in contact with water, yielding hydrochloric acid and magnesia. It has a sharp bitter taste, and is very soluble in water. A hot saturated solution deposits crystals containing 6 molecules of water, $MgCl_2 6H_2O$. This salt forms double salts with alkaline chlorides. It occurs naturally in sea water and in the water of many springs. Magnesium bromide, $MgBr_2$, which also occurs in sea water, in the water of salt springs, and of mineral springs, is likewise a very soluble salt.

MAGNESIUM CARBONATE.

Formula $MgCO_3$. Molecular Weight 84.

This substance has been known since the early part of the eighteenth century under the name of *magnesia alba*, but the distinction between it and calcium carbonate was first recognised by Black in 1755.

Occurrence.—Magnesium carbonate occurs naturally as magnesite, and in combination with calcium carbonate very abundantly as dolomite; it also occurs less frequently in combination with ferrous carbonate, as spherosiderite, and with manganous carbonate as dialogite.

Characters.—Magnesium carbonate, as prepared artificially, almost always contains water, and its composition is represented by the formula $MgCO_3 3aq$. The precipitate obtained by mixing solutions of sodium carbonate and magnesium sulphate is a compound of magnesium carbonate with magnesium hydrate, and the pharmaceutical preparation known as *magnesia alba* is of this nature, the relative proportions of carbonate and hydrate depending upon the strength of the solutions used, their temperature, and other conditions. It is a white earthy powder, very sparingly soluble in water. When prepared with cold dilute solutions it is extremely light and bulky, but when prepared with strong hot solutions it is much denser. At a red heat it gives off water and carbonic dioxide, leaving magnesium oxide or magnesia.

MAGNESIUM SULPHATE.

Formula $MgSO_4$. Molecular Weight 120.

This salt is commonly known as Epsom Salt, having been at one time obtained chiefly from the water of mineral springs in the neighbourhood of Epsom. It occurs abundantly in sea water and in the water of many mineral springs. It also occurs in a hydrated state as kieserite in the salt beds of Stassfurt and several other localities.

Characters.—Magnesium sulphate, as usually met with, is in the form of prismatic crystals containing 7 molecules of water of crystallisation; it dissolves in its own weight of cold water and in larger proportion in boiling water; it has a bitter unpleasant taste, and is highly purgative. When heated, 6 molecules of water are readily given off, but 1 molecule is retained even at 200°. At a red heat it becomes anhydrous, and is only partially decomposed at a very high temperature.

Preparation.—Magnesium sulphate is largely prepared by acting upon magnesian limestone with sulphuric acid, separating the sparingly soluble calcium sulphate by filtration, and evaporating the filtered liquid to crystallisation. It is also obtained as a by-product in the treatment of sea water for alkaline salts, and from the kieserite of Stassfurt.

ZINC.

Symbol Zn. Atomic Weight 65.

History.—This metal was known to the ancients only in the form of an alloy with copper, as brass; and although the existence of a peculiar metal in the ores used —together with copper ores—for obtaining this alloy was suspected by Basil Valentin and others, it was not generally recognised until the early part of the eighteenth century. The production of this metal on the large scale appears to have been carried out in England as early as 1730.

Occurrence.—Zinc seldom occurs naturally in the metallic state, but chiefly in a state of combination. It occurs in considerable abundance in the state of carbonate as calamine, and in the state of silicate as siliceous calamine; the sulphide also occurs very abundantly as blende; the oxide to some extent as red zinc ore, and combined with alumina and ferrous oxide as gahnite; the arsenate, phosphate and sulphate are also met with as minerals.

Characters.—Zinc is a bluish-white metal of considerable lustre when freshly polished, but readily becoming dull by oxidation when exposed to the air. It is brittle, and the fracture presents a crystalline texture. The density of zinc is 6·862, and by hammering it is increased to 7·210. Its malleability is increased by heating to 120° or 150°, sufficiently to admit of the metal being rolled into sheets, in which form it is used for a great number of purposes. At 210° it again becomes so brittle that it can readily be reduced to powder.

Zinc melts at 412°, and at a bright red heat it volatilises; it boils at 1040° and gives off vapour which in contact with air takes fire and burns with a very luminous flame, tinged with green and blue, forming a cloud of zinc oxide in the pulverulent form known as flowers of zinc. Zinc is not very subject to oxidation under atmospheric influences, and after the first film of oxide has been formed it seems to protect the metal from further alteration either by air or water, except when it is in contact with another metal and thus forms a galvanic circuit. Zinc dissolves readily in dilute acids, hydrogen being eliminated and salts of zinc formed which remain dissolved; it is also dissolved by alkaline solutions with evolution of hydrogen, and the zinc oxide thus formed combines with the alkali, forming a compound which is soluble in water.

Commercial zinc, commonly known as spelter, always contains small amounts of lead and iron, together with very minute quantities of carbon, tin, cadmium, copper and arsenic, which render the metal brittle and more difficult to roll into sheets than pure zinc. According to Karsten's experiments, lead is the most objectionable impurity, and even when it amounts to less than 1 per cent. it reduces the tenacity of the metal. Iron does not appear to affect the tenacity of zinc so much as lead, but it increases the hardness of the metal, and renders it more readily soluble by acids.

Preparation.—Zinc is obtained on the large scale by reducing the oxide with charcoal and distilling off the metal into suitable condensers. The ore used for this was formerly one of the two kinds of calamine, but more recently blende has been extensively worked as a source of zinc. It is first roasted to get rid of the sulphur and to convert the metal into the state of oxide; sometimes this roasting is conducted in such a way as to admit of the sulphurous oxide produced being used either for making sulphuric acid or some other purpose.

Roasting Ores.—Calamine is sometimes roasted in kilns, but more frequently reverberatory furnaces are used in roasting both calamine and blende. In the case of siliceous calamine the operation of roasting is chiefly useful in disintegrating the ore, but in the case of calamine consisting of zinc carbonate it has the further advantage of separating carbonic dioxide and water, which would otherwise interfere with the smelting operation by lowering the temperature, and thus retarding the reduction of the oxide. Blende requires to be crushed to a fine powder, and spread in a layer about 4 inches thick over the bed of the furnace, which is generally about 36 feet long by 9 feet wide, and is divided into

three parts, differing a few inches in height, the lowest portion being next to the fire bridge. When the furnace is sufficiently hot a charge of crushed ore is placed in the highest compartment of the bed and stirred from time to time so as to expose fresh surfaces to contact with the air, and thus facilitate the oxidation. After some hours this charge is raked down into the next compartment of the bed, and replaced by a fresh quantity of ore. After another interval the partially roasted ore is transferred to the lowest compartment of the hearth, and in this way successive charges of ore are worked through the roasting furnace.

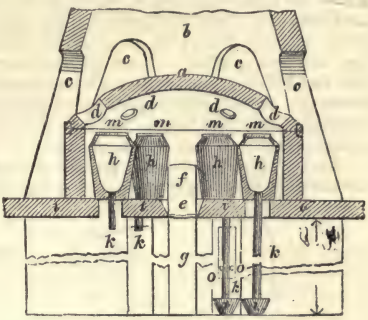


FIG. 205.

Reduction. — The roasted ore is mixed with half its weight of powdered charcoal or coal dust, placed in crucibles, retorts, or muffles, and heated sufficiently to effect the reduction and vaporisation of the metal. According to the English system, cast-iron crucibles are used in a circular furnace represented by figs. 205 and 206. The crucibles (*h h*) are closed above and have tubes passing through the bottom for the escape of the zinc vapour downwards. The sole (*i i*) of the furnace is perforated where the crucibles stand, to allow of the tubes being connected with sheet-iron pipes (*k k*) dipping into pots (*l l*) for receiving the condensed zinc. This operation is called distillation *per descensum*.

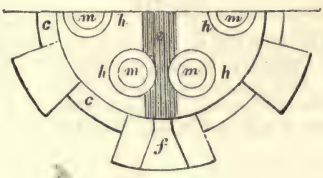


FIG. 206.

According to the Belgian system of smelting zinc, retorts are used for the reduction of the oxide. They are made of fire clay, as shown in fig. 207, and are 3 feet

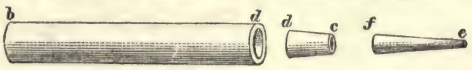


FIG. 207.

6 inches long from *b* to *d*, 7 inches in diameter; short conical pipes of fire clay (*d c*) are fitted into the necks, and to these are fitted conical tubes of thin sheet iron (*f e*).

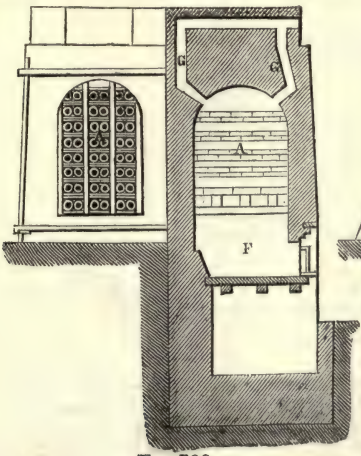


FIG. 208.

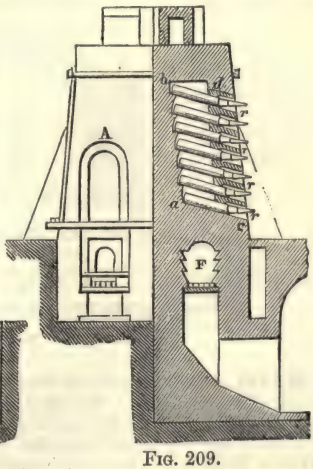


FIG. 209.

The furnace in which the retorts are heated is represented by figs. 208 and 209. F is the fireplace and A the chamber in which the retorts (*a c*, *b d*) are placed in a sloping position with the conical tubes (*r r*) adjusted to the mouths of the retorts.

When the retorts have been heated to a proper temperature they are charged with a mixture of calcined ore and carbonaceous material by means of a scoop, which fits

into the retorts, and the conical tubes are then fitted to the retorts with fire-clay luting. Carbonic oxide soon begins to escape and burn at the mouth of the conical tubes, and when the flame assumes a greenish-white colour, giving off white fumes, the sheet-iron cones are fitted on for the condensation of the zinc vapour. After some time the cones become filled with zinc oxide; they are then removed to clear out the oxide, and replaced as often as may be necessary. When a sufficient quantity of metallic zinc has collected in the conical clay tubes, it is scraped out into an iron ladle held under the mouths of the tubes and poured into moulds, this operation being repeated at intervals until all the zinc has been distilled off. The residue in the retorts is then drawn out and a fresh charge put in.

In the Silesian zinc works muffles made of baked clay (M, figs. 210 and 211) are used for the reduction; they are about 3 feet long and 20 inches high. At the front are

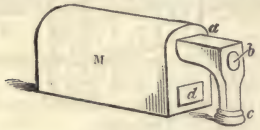


Fig. 210.



Fig. 211.

two holes, *a* and *d*; the lower one is intended for the removal of the residue left after each operation, and can be closed by a cover of fire clay while the distillation is going on. Into the upper hole is fitted a rectangular tube made of fire clay, which is open at the end (*c*) and has an aperture at *b* through which the muffle can be charged by means of a proper scoop. The furnace in which the muffles are heated is represented

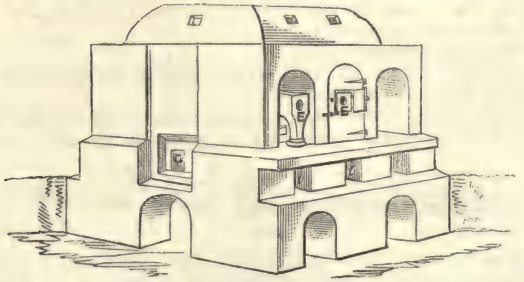


Fig. 212.

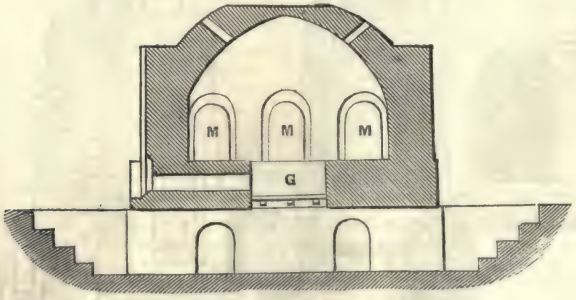


Fig. 213.

by figs. 212 and 213. Six or ten of these muffles are arranged in the apertures M M M and heated by the furnace G. The zinc vapour escapes through the rectangular pipes (E E) and passes into cavities (*o o o*), where it is condensed in iron pans.

The Silesian method of smelting zinc has been introduced in this country in place of the system formerly adopted, which was expensive on account of the large consumption of fuel it involved.

The zinc thus obtained is remelted in iron pots holding about half a ton each, the oxide collecting on the surface is skimmed off, and the metal cast into ingots for the market. Sometimes this operation is conducted in a reverberatory furnace, the hearth

of which is inclined to one side, where at the lowest point there is a hemispherical reservoir in which the liquid metal collects, the ingots of zinc to be melted being piled up on the highest part of the hearth near the fire bridge. The melted zinc is ladled out of the reservoir, and poured into moulds which have the form of slabs if the metal is required for rolling into sheets.

Uses.—Zinc is largely used in the form of sheet for purposes of construction, such as roofing, etc.; it is also much used for coating iron and producing what is termed galvanised iron. In order to coat iron with zinc the surface of the metal is first cleansed by immersing the sheets, or other articles to be galvanised, in a bath of dilute sulphuric or hydrochloric acid, and when perfectly free from oxide they are dipped into a bath of melted zinc on the surface of which is a layer of fat to prevent oxidation. The zinc then combines with the iron at the surface, forming an alloy which serves to protect the iron from oxidation and render it more durable.

Compounds.—Zinc is a divalent metal forming only one series of compounds. The oxide ZnO is a strong base, and the saline compounds it forms with acid oxides are isomorphous with magnesium salts; the chloride $ZnCl_2$ is a translucent fusible and volatilisable substance, very soluble in water, deliquescent and poisonous. A solution of this substance is used as a disinfectant under the name of Burnett's Fluid. Zinc chloride mixed with ammonium chloride is often used to clean metallic surfaces in soldering. Zinc sulphide, ZnS, is a white or yellowish-white substance insoluble in water; it is slowly acted upon by acids, with evolution of sulphuretted hydrogen, and is slowly oxidised when heated in contact with atmospheric air. It occurs naturally in the form of blende or black jack, is crystalline, of a dark yellow, brown, or black colour, and is one of the most important ores of zinc.

Zinc readily unites with other metals, forming alloys, most of which are hard and some of them brittle. Zinc and bismuth melted together do not form an alloy, but separate into two layers, the zinc containing about 2·5 per cent. of bismuth, and the bismuth from 8·5 to 15 per cent. of zinc. Alloys of zinc, tin, and copper constitute several kinds of bronze which, on account of their hardness, are well adapted for the journals and other parts of machinery. Some kinds of bronze contain lead as well as copper, tin, and zinc, such as British bell metal and the biddery ware of India.

The most important alloy of zinc is brass, which consists of zinc and copper in various proportions. The amount of zinc in brass ranges from 20 to 67 per cent. Muntz's yellow metal, or patent sheathing, is an alloy of this kind, consisting of 40 per cent. zinc and 60 per cent. copper. The alloy called similor contains a larger proportion of copper and white button metal more zinc.

ZINC OXIDE.

Formula ZnO. Molecular Weight 81.

History.—Zinc oxide was first proposed as a substitute for white lead by Courtois in 1780; in 1783 Gayton Morveau described its preparation, and showed the advantages it had over white lead; three years afterwards Courtois commenced preparing zinc white on a large scale. In 1796 Atkinson took out a patent in this country for the preparation of zinc white; but here as in France these earlier attempts to introduce the manufacture were not successful.

In 1849 the manufacture of zinc white was started again by Leclaire, and its establishment is due to him.

Occurrence.—Zinc oxide occurs naturally as zincite and franklinite, both of which contain also manganese oxides, and the latter ferric oxide and ferrous oxide in considerable amount. Franklinite occurs abundantly in New Jersey, and unsuccessful attempts have been made to work this ore for zinc. It is also smelted for iron, and it is said that the zinc contained in the iron thus obtained has the effect of giving greater tenacity to the metal.

Characters.—Zinc oxide obtained by burning zinc or igniting the carbonate is an amorphous flocculent substance which is largely used as a paint under the name of zinc white and for pharmaceutical purposes; it is insoluble in water; has a specific gravity of about 5·6; is very refractory in the fire, but is said to volatilise to some extent when very intensely heated. While hot it has a yellow colour, but becomes white again on cooling. Zinc oxide is very easily reduced by charcoal at a moderately high temperature, less readily by hydrogen or carbonic oxide. Heated with sulphur it forms zinc sulphide and sulphurous oxide. Chlorine displaces the oxygen at a red heat, forming zinc chloride and free oxygen. Zinc oxide is a strong base combining

readily with acid oxides and forming salts. It also combines with sesquioxides, such as alumina, chromic hydrate, and ferric oxide, and several of these compounds occur naturally.

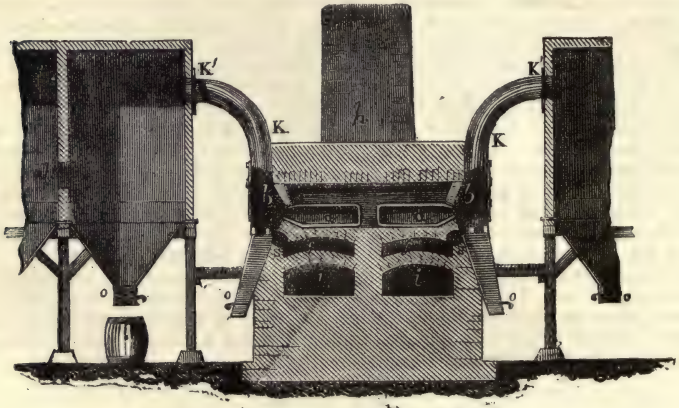
By adding ammonia or fixed caustic alkali to the solution of a zinc salt this oxide is obtained in the state of hydrate, ZnH_2O_2, as a gelatinous precipitate soluble in excess of the precipitant. When dried and heated it readily gives up its water. It can be obtained in a crystalline state from the ammoniacal solution of zinc oxide, and a dihydrate, ZnH_4O_3, is deposited slowly from a saturated solution of the oxide in caustic soda.

Preparation.—Zinc oxide is sometimes prepared by igniting the carbonate sufficiently to drive off the carbonic dioxide.

Attempts to prepare zinc oxide in the wet way have not as yet been commercially successful. Its manufacture on a large scale consists essentially in burning zinc vapour in contact with atmospheric air, and collecting the zinc oxide thus formed, in condensing tubes or chambers.

The furnace used in preparing zinc white is represented in vertical and horizontal sections by figs. 214, 215, and 217.

FIG. 214.



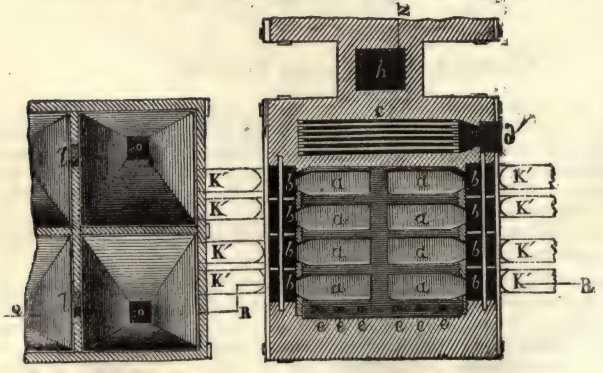


FIG. 215.

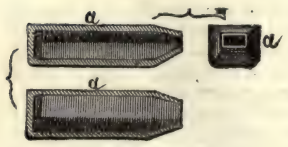


FIG. 216.

The metal is heated in fire-clay retorts (*a a*), 8 or 10 of which are placed together in the furnace (fig. 214). The shape of these retorts is shown by fig. 216. The length is 27 inches, the width 10 inches, height 6 inches, thickness of the walls $1\frac{1}{2}$ inch, height of the opening (*b b b*, figs. 214 and 215) 2 inches, width 4 inches.

The retorts are heated by the furnace (c, figs. 215 and 217), the flame playing round the retorts

and then passing through the flues (*c c f g*) into a chimney (*h*). Directly the retorts are heated to whiteness, each one is charged with 3 or 4 blocks of zinc, which melts, and the vapour escaping from the apertures (*b b*), coming into contact with air at a temperature of 300° C., transmitted from the channels (*s s*, fig. 214) towards (*b*), burns to zinc oxide, which is carried by the draught through the tubes (K K′) into a series of condensing chambers, where it is precipitated. The arrangement of the condensing chambers is shown by figs. 218 and 219. A is the retort furnace, H common chimney, B B tubes leading into the chambers. Each pair of tubes terminate in a system of four chambers. The inlet into the first chamber is above, and the outlet below; in the second chamber this is reversed. The outlet (M) of the last chamber is covered with a piece of wire gauze, to keep back as much as possible of the zinc white. After leaving this chamber, the gas passes through a long flue (G)

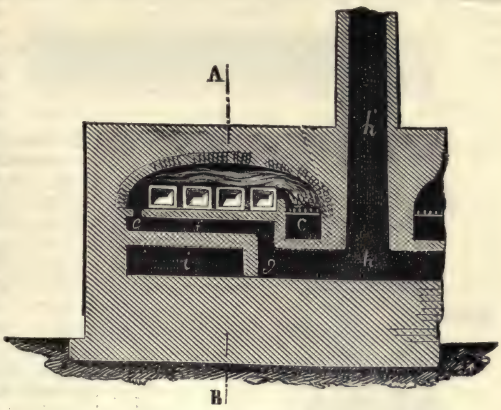


FIG. 217.

FIG. 218.

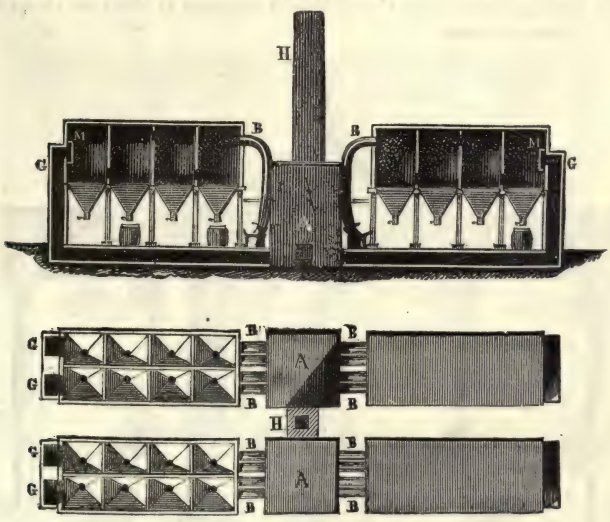


FIG. 219.

into the chimney (H). Wire-gauze partitions are often placed in the flue (G) to retain the zinc oxide. Most of the zinc white collects in the funnel-shaped parts of the condensing chambers, and is drawn out at intervals into the sacks or casks.

The zinc white deposited in the chamber is pure white, and only that portion deposited in the receiver (O) under the mouths of the retorts is a little grey, owing to the presence of a small quantity of metallic zinc. This greyish product, however, after being washed yields a product applicable for ordinary purposes.

Since zinc white is of a very loose and light nature, and consequently occupies a proportionately large space, it requires to be pressed into the barrels in which it is packed.

Figs. 220 and 221 represent another kind of retort for preparing zinc white. The

inner space is $3\frac{1}{2}$ feet long, 1 foot wide, and 4 inches high; the walls of the retorts are $1\frac{1}{4}$ inch thick at the bottom, and above $\frac{3}{4}$ inch. The opening (*a*) for putting in the zinc and for the escape of zinc vapour is 10 inches wide, and $1\frac{1}{2}$ inch high.



Fig. 220.



Fig. 221.

Two retorts of this kind are placed one above the other, as shown at (*a a*, fig. 222), with their mouths towards a common receiver, with a little bridge (*b*) at the side, which serves the purpose of separating the pure zinc white from that which is contaminated with particles of metallic zinc. This is deposited in front of the bridge (*b*) and falls down into the receivers (*b'b'*), while the pure product deposited in the conical tubes (*d d*) falls down through the space between *b* and *c* into the receivers (*c c*). Opposite the mouths of the retorts is a large iron door, which serves for removing damaged retorts and replacing them with new ones. This iron door is also furnished with smaller doors, opposite the mouth of each retort, through which the metallic zinc is thrown in.

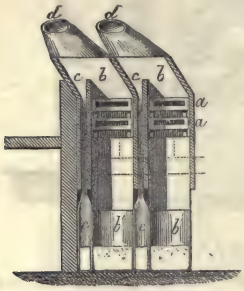


Fig. 222.

The retorts are placed in rows of 5 pairs together, or 10 in all over a common furnace; each retort of the lower row is charged with about $\frac{3}{4}$ cwt. of zinc, the retorts of the upper row each receiving half as much more. A single retort is capable of burning from 6 to 7 cwts. of zinc in the course of 24 hours. The coal required for this purpose is estimated at about 40–45 per cent. of the weight of the zinc used.

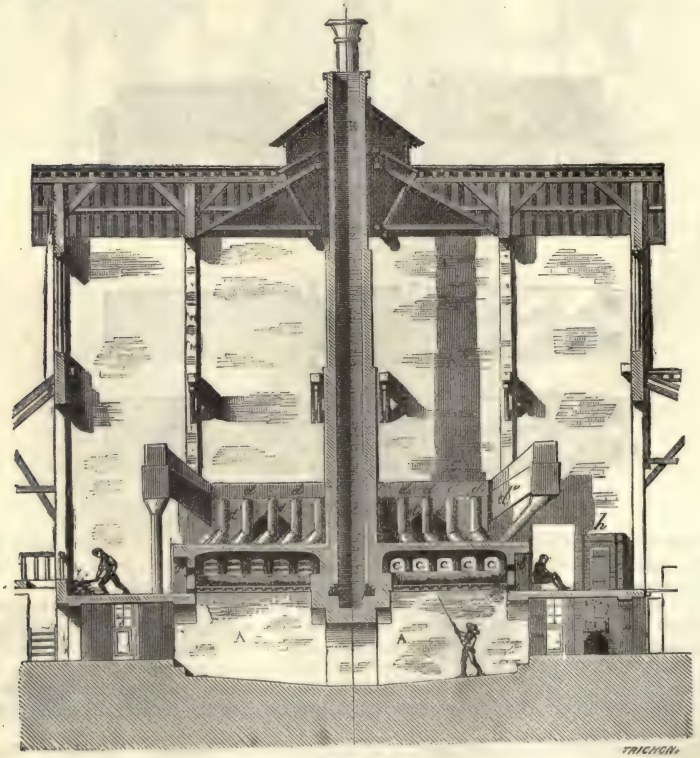


Fig. 223.

Fig. 223 represents in section a furnace with the retorts above described. The condensing chambers are shown in projection. (A A) ash pit, over which is a grate about 10 feet long, fed with coal through the fire doors (*b b*). The flame passes into the niches (*c c c*), in each of which are placed a couple of retorts, one above the other, as shown at the left hand of the drawing. The hot air, after having played round the retorts, passes through flues into the chimney (B). The burnt zinc vapour from each pair of retorts passes through the conical tubes (*d' d'*) to a flue (*d d*) of sheet iron, and then through upright tubes into a system of tubes shown in fig. 224, where A represents the ash pit, B the chimney for two series of furnaces, B' the retort furnaces, *c' c'* the tubes through which the heavy zinc white falls into the receivers beneath, while the lighter sort passes into the tube (*d*). The hot air with the suspended particles of zinc white then passes through the siphon-shaped metal tubes ($d'' d''' d^4 d^5$), which terminate at their lower extremities in the receivers ($e e' e'' e''' e^4$). These receivers have funnel-shaped bottoms, in which the zinc white deposited in the tubes collects, and falls into sacks placed beneath. These siphon-shaped tubes (*d'' d'''*) may be arranged in pairs side by side, and carried round the whole of the building. Considerable quantities of zinc white are deposited in these tubes, and the hot air from them is passed into the chambers on the side of the building opposite to the furnaces, in order to collect the last particles of zinc white. The arrangement of the condensing chambers is represented in vertical section lengthways by fig. 225, six of them being placed together, 3 to each furnace, as shown in fig. 226. The gas cooled to 50° in the tubes, passes from the receiver (*f''*) into the first chamber (*g g'*), lined with plush linen,



Fig. 224.

and divided into two parts (*g g'*) by a partition, reaching not quite to the top. From the first chamber the gas passes from below into the first division (g^2) of the second chamber, then over the partition into the second division (g^3), then into the third chamber ($g^4 g^5$), and so on until it reaches the eighth. It then passes into a second series of 8 chambers, afterwards into a third similar series of chambers, and from the eighth chamber of this series it escapes through a curtain of wire gauze into the chimney (g^{15}). Each chamber terminates below in a funnel, where the zinc white collects and is drawn off into casks.

Reckoning together the tubes and chambers, the products of combustion of each furnace with ten retorts travel a distance of nearly 1000 yards. In the 40 retorts of a furnace with four sets of retorts, the quantity of zinc burnt in 24 hours may be reckoned at about 12 tons; 3000 tons in the year of 250 working days.

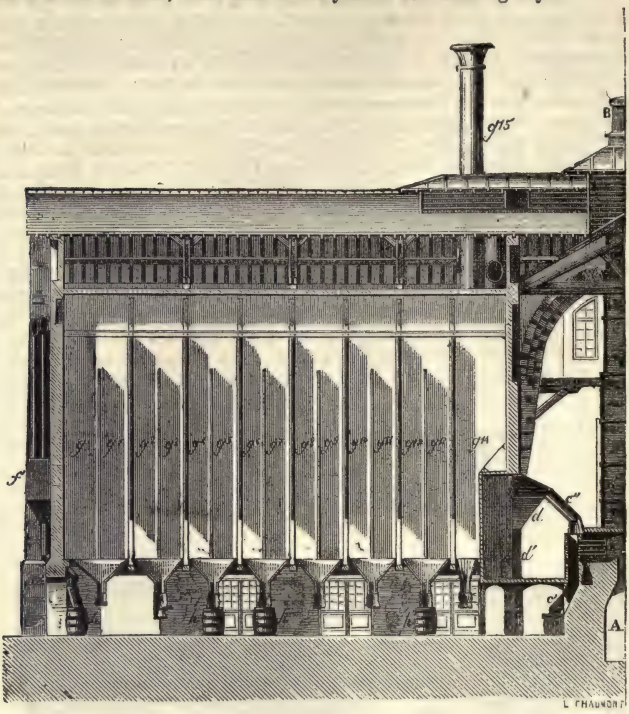


FIG. 225.

Fig. 226 represents a horizontal section of the retort furnaces, condensing tubes and chambers. A A four series of retort furnaces, *b b* receivers, *d d' d''* . . . *d*⁸ funnel-shaped receivers for the siphon-shaped condensing tubes, out of which the gas passes into the chamber system opposite to the retort furnaces.

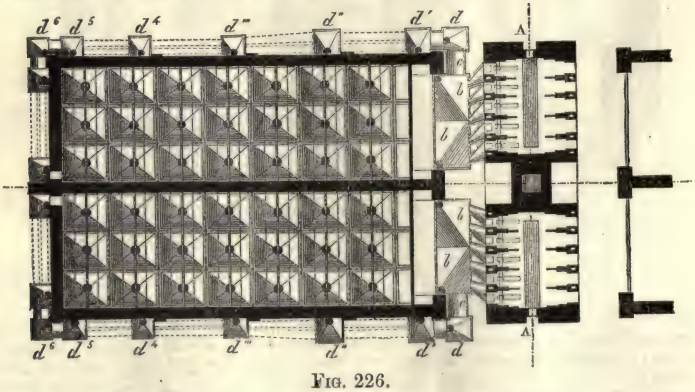


FIG. 226.

The products of this apparatus are: 1. Zinc dust, consisting of a mixture of zinc white and finely-divided metallic zinc, which is purified by a special washing process. 2. Zinc white, which is removed from the receivers every morning. The

products deposited in the different receivers vary in tint. In order to render the zinc white uniform, the contents of the different receivers are well mixed together in some suitable vessel before being packed into casks for transport.

At Grenelle a different method is adopted, and the zinc is burnt in fire-clay crucibles (B, figs. 227 and 228), instead of retorts. A is the support for the crucibles in the furnace, C the lid with an opening D, 2 inches in diameter, for throwing in the zinc and for the escape of zinc vapour. Figs. 229 and 230 represent a crucible furnace with 7 crucibles. The ashpit beneath the grate is closed at pleasure by the door (*f*). When closed, hot air passes through the flue (*f'*) under the grate. The flame plays round the 7 crucibles (*h h*), and escapes through the flue (*a*) to the chimney. Above each crucible is an opening large enough for removing broken crucibles and replacing them with new ones; the opening is generally closed by the lid (*k*). At the part of the furnace (*b c*) shown in projection in fig. 229 there are iron doors (*i i*), and small openings (*j j*), which serve to admit and regulate the supply of air required for the combustion of the zinc vapour. Opposite the mouth of each crucible is an opening (*m*), through which the gas passes, together with zinc white, into the tube (*q r*), then into the condensing chambers. Between the opening (*m*) and the tube (*q*) are two cavities (*o* and *p*), in the first of which is deposited zinc dust, and in the second impure zinc white. Beneath the tube (*q r*) is a sliding damper for drawing off the zinc white deposited at *q* into a vessel (*v*).

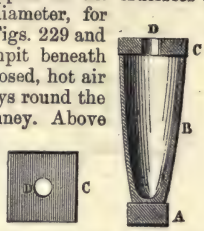


Fig. 228.

Fig. 227.

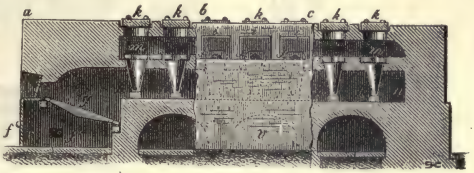


Fig. 129.

Preparation from Zinc Ores.—The preparation of zinc white from calamine, red zinc ore, or blende, has not at present attained any importance, since the product thus obtained is deficient in whiteness. The ores most suitable for conversion into zinc white are those which contain zinc oxide, such as calamine, red zinc ore, and franklinite; blende is less suitable. The essential feature of the process consists in heating the ore to redness with coal in muffle-shaped furnaces, the zinc vapour thus produced being burnt to zinc white.

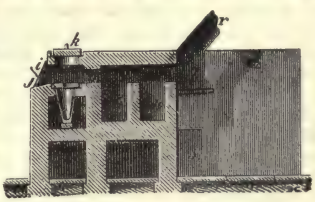


Fig. 230.

The zinc white deposited in the first receivers of the furnaces has a greyish tint, owing to an admixture of finely-divided metallic zinc. In order to separate this, the product is submitted to a process of elutriation, in an apparatus represented by fig. 231. *a* is a water tank from which the flow of water into the box (*c*) is regulated by the cock (*b*). The impure zinc white is placed in the

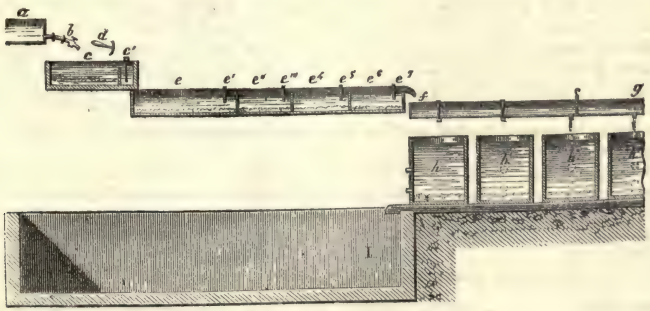


Fig. 231.

box (*c*) and stirred with a rake (*d*), while water flows in from the tank (*a*). The water, retaining zinc white in suspension, flows over a partition through a hair sieve

(c') into the trough (e), then under the partition (e') over the next partition (e''), and so on to the partition (e^4), etc., till it reaches the partition (e^6), and passes through a channel into the large basin (I), where the zinc white still retained in suspension is deposited after some time. From e^6 the liquid flows into the long settling trough ($f\,g$), the bottom of which has a number of perforations closed with wooden plugs. Beneath these openings are placed a corresponding number of vats ($h\,h'\,h''\,h'''$) into which the zinc white deposited in the trough is let out. After remaining here for eight days, the supernatant water is drawn off, and the pasty zinc white, as well as that in the boxes ($e\,e''\,e^4\,e^6$) removed to filters consisting of linen bags ($a\,a\,a$, fig. 232), supported upon wooden frames. After the water has drained off, the stiff pasty zinc white remaining in the filter must be dried as quickly as possible by the application of heat. When slowly dried the mass becomes so hard that it is difficult to break up.

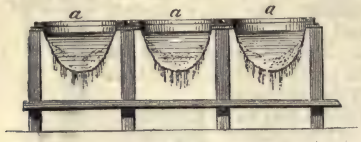


FIG. 232.

The drying apparatus is represented by figs. 233 and 234, and consists of a cast-iron pan (b) about 50 feet long and 8 inches deep, supported upon a thin bed of bricks

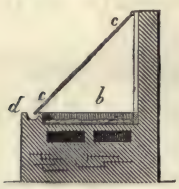


FIG. 233.

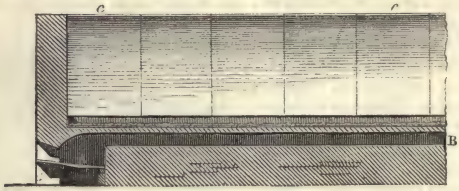


FIG. 234.

beneath which pass two flues from the furnace (A). The metal lids ($c\,c$), turning on hinges, are for the purpose of observing the progress of the drying as well as for stirring the mass. The water condensing on the lids runs off by the channel (d). The pasty zinc white is spread out upon the pan (b), 3 or 4 inches deep, and kept there until completely dry. Instead of applying direct heat, the hot air from a zinc white furnace may be made to pass under the drying pans. The dried zinc white is broken up, pressed through a fine sieve, and packed.

Latry in Grenelle separates the metallic zinc from zinc white by boiling the zinc dust in a cauldron with water, by which means the zinc white is brought into suspension, and carried with the water through a side opening into settling tanks, while the metallic zinc settles to the bottom even in the boiling water and remains in the cauldron.

SICCATIVE FOR ZINC WHITE.—White lead paint is rendered drying by mixing it with linseed oil that has been boiled with litharge. This plan does not answer in the case of zinc white, because the chief advantage of zinc white, of not blackening in an atmosphere of sulphuretted hydrogen, would then be lost. Leclaire prepares a drying oil to be used with zinc white by boiling linseed oil with manganese peroxide. 100 parts of well-boiled and purified linseed oil and 5 parts of well-ground manganese peroxide are heated with frequent stirring nearly to boiling. Instead of mixing the manganese peroxide with the oil, it may be suspended in a bag in the heated oil. The manganese peroxide remaining, as the case may be, either in the bag or at the bottom of the boiling vessel, when exposed to the air, acquires the property of rendering oil drying in a greater degree, so that the same manganese peroxide serves for any number of operations.

According to Sirel, a very good dryer for zinc white is obtained by intimately mixing manganese subchloride—completely freed from iron by means of potassium ferrocyanide—with 19 parts of zinc oxide or barium sulphate; and 2 per cent. of this mixture, added to zinc white, is sufficient to make the oil paint thus prepared dry in 36 hours.

The Vielle Montagne Company employs the following dryers:

Zinc white . . .	980 parts	Manganous acetate .	6·66 parts
Manganous sulphate .	6·66 „	Zinc sulphate . .	6·66 „

These materials in a fine state of division are intimately mixed, and 2 per cent. of the mixture added to the zinc white in making paint.

Barruel's dryer consists of zinc white and 5 to 6 per cent. of manganous borate. Rochaz's dryer is made of 20 parts zinc white, 6 parts pine resin, 2 parts turpentine, and 1 part boiled linseed oil; or, 20 parts zinc white, 3 parts Burgundy pitch, and 1 part boiled linseed oil.

Preparation of Zinc White Oil Colours.—For preparing zinc white paste, the dry zinc white is mixed with 4·8 per cent. of dryer and 48 per cent. linseed oil. Paint ready for use is made by mixing together zinc white with 76 per cent. linseed oil, 4·8 per cent dryer, and 8 per cent. of turpentine.

When the surface to be covered has a strong tendency to absorb, as is the case with plaster of Paris walls, etc., the quantity of oil used in the first coating is increased threefold. The use of much turpentine is to be avoided, not only on account of the slow rate of evaporation, the unpleasant smell, and the formation of a resinous coating, but also because it leaves the zinc white in such a loose condition that it adheres very badly. Benzin may be used instead of turpentine when desired.

Zinc white admits, like white lead, of being made into an oil colour while in a moist condition; the oil displaces the water, which may be easily drawn off.

The following table gives the percentage amounts by weight of different pigments requisite for producing different tints with zinc white:

Azure blue	1 part	indigo
Pearl blue	1 „	charcoal
Slate blue	100 parts	zinc dust
Straw yellow	2·5 „	zinc or lead chromate
Chamois	3 „	yellow ochre and 3 parts cinnabar
Lemon yellow	2·5 „	chrome yellow and 2½ parts Prussian blue
Gold colour	10 „	chrome yellow
Water green	8 „	Prussian blue
Grass green	100 „	chrome yellow and 8 parts Prussian blue
Olive green	50 „	yellow ochre and 12 pts black
Bronze green		chrome yellow, 6 parts Prussian blue and 6 parts black

The black employed is either ivory black, bone black, lamp black, or manganese peroxide, etc.

Uses.—Zinc white admits of being substituted in all cases for white lead, and its use is advantageous in all cases where the atmosphere is liable to contain sulphuretted hydrogen. Besides the use of zinc white in the preparation of printed goods, writing paper, wall paper, cards, wood, stone, and gypsum painting, etc., it has of late been used for stopping teeth when mixed with zinc chloride; it is used for polishing optical glasses, for decolorising glass, for preparing artificial meerschaum, for printing loose fabrics so as to give them the appearance of lace or embroidery work.

ZINC SULPHIDE.

Formula ZnS. Molecular Weight 97.

History.—This substance occurring naturally as blende, was first shown to be an ore of zinc in 1735 by Brandt; prior to that time it had been regarded as a useless lead ore, *galena inanis*. It is now one of the chief sources of metallic zinc.

Occurrence.—Zinc sulphide occurs very abundantly in various geological formations, frequently associated with galena, heavy spar, copper pyrites, spathic iron, and silver ores.

Zinc sulphide is a constituent of several metallurgical products, as, for instance, copper regulus; it gives rise to the formation of accretions in the furnaces where lead or copper ore is smelted.

It also occurs, combined with various other sulphides, in some of the varieties of fahl-ore.

Characters.—Zinc sulphide when pure is colourless, and in the crystalline state transparent or translucent; the sulphide obtained by precipitation is white and pulverulent. As it occurs naturally it has more frequently a yellow, brown, or black colour, owing to the presence of impurities; and the mass has either a scaly crystalline texture or is granular and compact. Blende often contains a large amount of iron in

the state of sulphide, and has then a black colour, on which account it is termed black jack.

	New Jersey	Clausthal	Carinthia	New Hampshire	Tuscany
	Henry	Kuhlemann	Kersten	Jackson	Becchi
Sulphur . . .	32·22	33·04	32·10	32·6	33·65
Zinc . . .	67·46	65·39	64·22	52·0	48·11
Cadmium . .	—	0·79	trace	3·2	—
Iron . . .	—	1·18	1·32	11·3	16·23
Copper . . .	—	0·13	0·72	—	—
Lead . . .	—	—	0·80	—	—
Antimony . .	—	0·63	—	—	—
	99·68	101·16	99·16	99·1	97·99

Zinc sulphide in the form of blende requires a very high temperature for melting, and it volatilises at a white heat; it oxidises but slowly when heated in contact with atmospheric air, and less readily than most other sulphides. Sulphurous oxide is given off, and there is formed a mixture of zinc oxide with zinc sulphate, from which greater part of the sulphuric oxide is given off at a higher temperature. Part of the zinc sulphide always remains unoxidised. By fusion with nitre zinc sulphide is easily and completely converted into sulphate; it is decomposed slowly by acids with evolution of sulphuretted hydrogen. The amorphous hydrated sulphide obtained by precipitation, $ZnS.H_2O$, oxidises very rapidly on exposure to the air, and is dissolved very readily by acids even when dilute.

ZINC SULPHATE.

Formula $ZnSO_4$. Molecular Weight 161.

History.—This salt, commonly known as white vitriol or white copperas, was certainly manufactured as an article of commerce at Goslar in the Hartz about the middle of the sixteenth century; but it was mentioned at an earlier date by Basil Valentin, and was probably known long before that time. The relation of white vitriol to zinc and calamine was partially recognised by Geoffroy in 1713, but its composition was not established until 1735, when Lemery pointed out that it was different from green vitriol or ferrous sulphate, and Hellot prepared it by dissolving zinc with sulphuric acid. Shortly afterwards Brandt demonstrated that this salt contained zinc, both by preparing it from the metal and by making brass by melting the calcined salt with charcoal and copper.

Occurrence.—Zinc sulphate occurs naturally as goslarite at several places, together with blende, and is probably a product of the oxidation of this mineral. A considerable quantity of zinc sulphate is now obtained as a secondary product.

Characters.—Zinc sulphate is colourless, has an astringent metallic taste, and is a powerful irritant poison; it is readily soluble in water and usually crystallises with 7 molecules of water in right rhombic prisms, which effloresce in dry air, give off 37·6 per cent. or 6 molecules of water at about 100°, but retain 1 molecule until heated up to 260°. At a full red heat the dry salt is decomposed, giving off sulphuric oxide, which is partially converted into sulphurous oxide, and yielding zinc oxide, which remains as a white powder. The crystalline salt dissolves in less than its weight of boiling water and rather more than twice its weight of cold water; it is quite insoluble in alcohol.

Preparation.—Zinc sulphate may be prepared by dissolving either zinc or the oxide or carbonate in dilute sulphuric acid, and it is made on the large scale by roasting the native sulphide or blende until it is converted into sulphate by oxidation, then dissolving out the salt with water, and evaporating the solution to dryness. Since the blende used for this purpose generally contains other minerals, the salt obtained in this way is impure, containing iron, copper, lead, etc.: it is therefore slightly calcined to oxidise ferrous sulphate, redissolved in water, and the solution left in contact with plates of metallic zinc until the foreign metals are precipitated; the clear colour-

less solution is then evaporated down to a small bulk, and on cooling the zinc sulphate separates in small crystals as an opaque white granular mass.

Uses.—Zinc sulphate is used in medicine, as a mordant in dyeing, in calico-printing, and in the preparation of drying oil for painting.

ZINC CHLORIDE.

FORMULA $ZnCl_2$. MOLECULAR WEIGHT 136.

This salt is a white translucent solid, fusible without decomposition when anhydrous, and volatile at a red heat. It is very soluble in water and deliquesces when exposed to moist air; it is also soluble in alcohol. The specific gravity is 2·753.

Zinc chloride may be prepared by dissolving zinc in hydrochloric acid and evaporating the solution to dryness, or by heating the metal in an atmosphere of chlorine gas.

Zinc chloride combines with ammonium chloride and other chlorides, forming double salts; and with albumen or gelatin it forms sparingly soluble compounds. A solution of zinc ammonium chloride is much used in soldering for the purpose of removing oxide from the surface of the metals. Zinc chloride in the solid state has a powerful corrosive action on the skin and is used as a caustic; in solution it is used for preserving wood, and as a disinfectant, the action in both cases being due to the combination of the salt with albuminous and gelatinous substances. Burnett's Disinfecting Fluid is a strong solution of zinc chloride; it is highly poisonous.

ZINC CARBONATE.

FORMULA $ZnCO_3$. MOLECULAR WEIGHT 125.

History.—This substance as it occurs naturally was probably known at a very early period, under the name of calamine, as the earth by which copper was coloured yellow in the production of brass. The term calamine, however, was applied not only to the carbonate but also to the silicate of zinc; and for a long time these two minerals compounded together were the only source from which metallic zinc was obtained.

Occurrence.—Zinc carbonate occurs naturally both crystallised and as granular or earthy masses; when pure it is colourless, transparent, or translucent, but is more frequently coloured by the presence of iron, manganese, copper, etc.

	Somerset-shire	Kobell	Aix-la-Chapelle				Mexico
	Smithson		Monheim				Genth
Zinc oxide . .	64·8	96·00	60·35	55·89	34·92	74·42	93·74
Carbonic dioxide .	35·2						
Ferrous carbonate .	—	2·03	32·31	36·46	1·58	3·20	—
Lead „ .	—	1·12	—	—	—	—	—
Manganous „ .	—	—	4·02	3·47	6·80	14·98	1·50
Calcium „ .	—	—	1·90	2·27	1·58	1·68	1·48
Magnesium „ .	—	—	0·14	—	2·84	3·88	0·29
Cupric „ .	—	—	—	—	—	—	3·42
Zinc silicate . .	—	—	2·49	0·41	1·85	—	—
Silica . . .	—	—	—	—	—	0·20	—
Water . . .	—	—	—	—	—	0·56	—
	100·00	99·15	101·21	98·50	99·57	98·92	100·43

Characters.—Zinc carbonate is colourless and insoluble in water, it is decomposed slowly at 300°, and readily by a red heat, and giving off carbonic dioxide is converted into zinc oxide. As usually obtained, by grinding and washing native calamine, it presents the appearance of a pale flesh-coloured powder; the colour, however, is merely due to the presence of accidental impurity, generally iron or manganese.

Preparation.—The precipitate obtained by mixing solutions of zinc salts and fixed alkaline carbonates is not zinc carbonate, but a mixture or compound of the car-

bonate with zinc hydrate, and the only method of preparing neutral zinc carbonate is to dissolve the precipitate by charging the liquid with carbonic dioxide, and to evaporate the solution in an atmosphere of the gas.

The substances precipitated from solution of zinc salts by alkaline carbonates differ in composition according to the nature, strength, and temperature of the solutions used. Cold concentrated solutions yield a precipitate containing less carbonic acid than that formed in very dilute cold solutions or in boiling solutions.

A similar hydrocarbonate occurs naturally as zinc bloom, and in combination with copper compounds as aurichalcite and buratite.

All these hydrocarbonates give off water and carbonic dioxide at 200°, yielding zinc oxide ZnO. The precipitate produced by a fixed alkaline carbonate dissolves in solution of ammonic carbonate and yields, on evaporation, crystals of a double salt. Similar double salts containing potassium and sodium can be obtained.

The native zinc silicate, which is so often confounded with the carbonate, occurs both crystallised and compact, frequently associated with the native carbonate. It is white when pure, but generally coloured in consequence of the presence of ferric oxide or other impurities. A specimen analysed by Rammelsberg had a composition corresponding to the formula $2ZnO.SiO_2 + H_2O$. Part of the zinc is sometimes replaced by iron or lead.

Anhydrous zinc silicate often occurs as willemite in deposits of zinc ores, and very abundantly in New Jersey; a variety called troostite occurs associated with franklinite in the same locality.

ZINC ACETATE.

Formula $Zn2(C_2H_3O_2)$. Molecular Weight 183.

The salt dissolves in three times its weight of cold water and half its weight of boiling water, crystallises with 3 molecules of water, melts at 100°, and gives off its water with partial decomposition. It is used by dyers as a mordant, and is often prepared for that purpose by mixing solutions of zinc sulphate and of lead acetate, which decompose each other according to the following equation:

$$ZnSO_4 + Pb2(C_2H_3O_2) = PbSO_4 + Zn2(C_2H_3O_2).$$

The clear liquid drawn off from the precipitated lead sulphate is then evaporated until sufficiently concentrated to crystallise on cooling.

CADMIUM.

Symbol Cd. Atomic Weight 112.

This metal was discovered by Stromeyer in 1817, and about the same time by Hermann. It occurs either as sulphide, carbonate, or silicate, associated with zinc ores in small amounts, and its name is derived from the term *cadmia fossilis* by which calamine was formerly known.

Cadmium is a white metal resembling tin in appearance; its density is 8·604, and after hammering 8·694; it is very malleable, melts at a red heat, and is very volatile. Like zinc, it is divalent, and forms but one series of compounds; the oxide CdO has a pale brown colour, is infusible, and absorbs carbonic dioxide, forming carbonate. The chloride, bromide, and iodide are soluble salts. The sulphide CdS is a bright yellow crystalline powder, that is used as a pigment on account of its fine colour. It occurs naturally as greenockite. The other salts and compounds of cadmium present considerable analogy with those of zinc in character and composition.

LEAD.

Symbol Pb. Atomic Weight 207.

History.—The earliest definite mention of this metal is to be found in the works of Pliny, who called it *plumbum nigrum*, and thus distinguished it from another metal called *plumbum candidum* or *album*, which was probably either tin or an alloy containing tin; but, prior to that time, the two metals appear to have been frequently confounded together under the name *μόλιβος*. Lead was used by the Romans for making water pipes, and its ores were worked by them both in Spain and in this country.

Occurrence.—Lead does not occur naturally in the metallic state to any great extent, but the compound with sulphur occurs abundantly as galena, and combined in several proportions with antimonous sulphide, as zinkenite, plagionite, jamesonite, feather ore, boulangerite, geokronite, kilbrikenite; with antimonous sulphide and cuprous sulphide as bournonite; with cuprous sulphide and bismuth sulphide as needle ore, and with some other sulphides. Lead also occurs in the oxidised state as minium, as peroxide and litharge; the sulphate as lead vitriol, the carbonate as white lead ore, and in combination with the sulphate as leadhillite and sulphato-carbonate, the tungstate as scheeletine, the molybdate as wulfenite, the chromate as melanochroite, the aluminate as lead gum. Lead also occurs in combination with chlorine as cottunite, and the chloride occurs combined with the phosphate and arsenate as pyromorphite, combined with the carbonate as horn lead, and combined with the oxide as mendipite.

The most abundant ore of lead is galena, and it almost invariably contains silver, the amount varying from mere traces up to such proportions that this ore is an important source of silver.

Characters.—Lead has a bluish-grey colour and considerable lustre when free from the thin film of oxide which is readily formed by contact with atmospheric air. The metal is so soft that it can be easily scratched or cut with a knife; it is very malleable and ductile when pure, and can be rolled into very thin sheets or drawn into wire; but these characters are considerably modified by the presence of very small proportions of other metals or of lead oxide. The tenacity of lead is but slight, and a wire $\frac{1}{12}$ inch diameter will not support a weight of 20 pounds. The specific gravity is about 11·35 or 11·44.

Lead melts at 325° to 335°, and at a red heat it volatilises; its specific heat is 0·0314, and it has a low conductive power for heat and electricity. When exposed to dry air or to water free from air it is not altered, but in contact with moist air it is rapidly covered with a film of oxide; and in water containing air and carbonic acid it soon becomes covered with a white coating of carbonate and hydrate, which is partially dissolved by the water.

Heated in contact with air lead assumes at the surface an iridescent appearance as a result of oxidation, and it is soon covered with a yellowish coating of oxide. When the temperature is sufficiently high to melt the oxide, it is absorbed by the unoxidised metal, which then becomes dull and brittle.

Acids which do not readily yield oxygen do not act upon lead except when it is also in contact with air; moderately dilute nitric acid dissolves lead very readily, forming a nitrate. Strong sulphuric acid converts it into sulphate when heated to the boiling point, but when the acid is dilute it has little action upon lead; hydrochloric acid has but little action upon lead. Weak acids like acetic acid exert a considerable solvent action upon lead, especially when it is in contact with atmospheric air; and on this account leaden vessels are not fit to be used in the preparation or preservation of articles of food containing acids.

The action of water upon lead is of great importance in a sanitary point of view, since this metal is extensively used for cisterns and water pipes. Water containing only a small amount of saline substances, such as sulphates, carbonates, or phosphates,

does not dissolve the lead oxide formed on the surface of the metal, and water containing acid calcium carbonate does not act upon lead to any appreciable extent after a film of lead carbonate has been formed on its surface. With water free from saline impregnation, but containing carbonic acid, like rain water, the case is very different; since lead carbonate is dissolved by the carbonic acid sufficiently to cause a dangerous contamination of the water.

Preparation.—Since galena is the most abundant ore of lead and the most important source of this metal, the various operations of lead smelting are chiefly regulated in accordance with the chemical characters of lead sulphide. The ores—consisting either wholly or in part of carbonate, sulphate, phosphate, or other oxy-salts of lead—require somewhat modified treatment; but such ores do not furnish more than one-tenth part of the material used in the production of lead.

Lead ores, however, frequently contain admixtures of other minerals, some of which —like fluor spar, quartz, calc spar, or barium sulphate—do not yield metal in the process of smelting and are comprised under the general term gangue; while others, like pyrites of different kinds, blende, etc., contain metals which are reduced together with the lead and remain alloyed with it. In many instances such a result would not be desirable, and therefore such lead ores are submitted to mechanical operations of picking and sorting before being smelted, in order to separate as far as possible the admixtures from the galena. Very often, however, the foreign minerals are intimately mixed with the galena, or even combined with it, so that their separation by mechanical means is impracticable; and in such cases the operations of smelting are modified in certain details with the view of effecting the separation of the lead from the other reducible metals associated with it. Sometimes the subsidiary operations carried out for this object are extremely complicated.

As regards the extraction of lead from galena, the operation of smelting, as most frequently carried out, is based upon the behaviour of lead sulphide when heated together with lead oxide; mutual decomposition takes place, the sulphur combining with the oxygen of the lead oxide to form sulphurous oxide gas, while the lead of both substances is separated in the metallic state, according to the following equation:

$$\begin{array}{cccccccc} PbS & + & 2PbO & = & 3Pb & + & SO_2 \\ 239 & & 446 & & 621 & & 64 \end{array}$$

A precisely similar reaction takes place when lead sulphide is heated together with lead sulphate; and in this case also the products of the chemical change are sulphurous oxide and metallic lead, according to the following equation:

$$\begin{array}{cccccccc} PbS & + & PbSO_4 & = & 2Pb & + & 2SO_2 \\ 239 & & 303 & & 414 & & 128 \end{array}$$

When lead sulphide is heated in contact with atmospheric air, it is gradually oxidised, sulphurous oxide is given off, and the lead eventually remains partly in the state of oxide and partly as sulphate, as shown in the following equation:

$$\begin{array}{cccccccccc} 2PbS & + & 7O & = & SO_2 & + & PbO & + & PbSO_4 \\ 478 & & 112 & & 64 & & 223 & & 303 \end{array}$$

Consequently, the substances requisite for effecting the separation of sulphur from galena so as to obtain the lead in the metallic state may be produced by operating upon the ore in such a manner as to effect the oxidation of part of the lead sulphide and the formation of lead oxide and lead sulphate sufficient to decompose the lead sulphide that remains unoxidised. The smelting of rich lead ores consisting of galena is, in most instances, effected in this way, and sometimes the operation is carried out in two distinct stages, in the first of which, termed the calcination, the finely powdered ore is exposed to the action of atmospheric air at a moderate heat, and constantly stirred about meanwhile, until the sulphide has been oxidised to a sufficient extent. The true smelting of the ore, or the reduction of the metal it contains, is effected in the second stage of the operation, and it requires a much higher temperature than the calcination.

It is obvious that, in order to obtain the whole amount of lead contained in the ore operated upon, the proportion of lead sulphide oxidised should bear exactly the relation to the unoxidised portion that is indicated by the equations given above. Practically it would be impossible to obtain such a result even with ore consisting of pure galena; and in all cases some portion of the lead remains, either in the state of sulphide, or as oxide, sulphate, etc. Besides, lead ores always contain, together with galena, other substances which must be separated in the smelting, either as slag or otherwise; and the conditions under which this result is brought about also determine the formation of lead compounds, which escape reduction and remain in the slag or other by-products. In this way it happens that in smelting lead ore there are obtained,

besides metallic lead, various other products containing an amount of the metal sufficient to be worth extracting by further treatment.

Another method of smelting lead ores is based upon the action of metallic iron upon lead sulphide at a high temperature, as shown in the following equation:

PbS	+	Fe	=	FeS	+	Pb
239		56		88		207

A portion of the lead sulphide combines with the ferrous sulphide formed, producing a regulus approximating to the composition FeS + PbS.

Ferrous silicate, in the form of slag from iron-refining or from copper-smelting works, is sometimes substituted with advantage for metallic iron for the reduction of lead from galena, by smelting a mixture of the ores and slag in contact with coke in a blast furnace.

The coarser kinds of ore containing, besides galena, admixtures of iron pyrites or other sulphides in considerable amount, yield, when smelted with scrap iron, only a small proportion of metallic lead, together with a large quantity of regulus rich in lead. To render such ores more suitable for smelting they are often submitted to a preliminary roasting, either in open heaps, stalls, or reverberatory furnaces, by means of which the sulphur, arsenic, antimony, zinc, etc., are partially volatilised, and the other sulphides are partially converted into oxides, which can be dissolved by melting the roasted ore with siliceous slag in contact with reducing agents, while the more easily reduced lead oxide yields metallic lead. A certain proportion of lead regulus is generally formed at the same time by the reduction of the sulphates into which the sulphides are partly converted in the roasting operation.

At Freiberg the lead ore is roasted in a finely divided state in reverberatory furnaces until the amount of sulphur remaining does not exceed 5 per cent.; and the following analysis by Mrázek represents its composition after roasting:

Silica	17·4
Alumina	1·8
Lime	2·0
Magnesia	0·5
Ferrosoferric oxide	33·3
Zinc oxide	16·0
Manganous oxide	trace
Lead oxide	22·0
Cupric oxide	0·3
Antimonic oxide	trace
Arsenic oxide	1·1
Sulphuric acid	trace
Sulphur in sulphides	3·62
Silver	0·13
	98·15

The arrangement of the roasting heap in the Lower Hartz and in Sweden is represented in vertical section by fig. 235. A thick rectangular bed of pine wood (*a a*) is

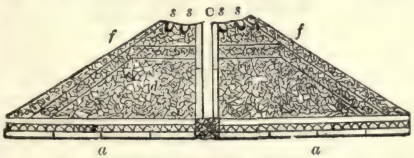


FIG. 235.

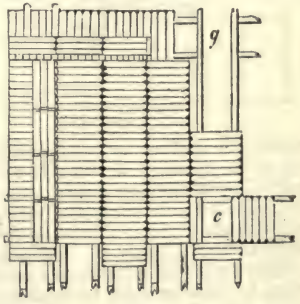


FIG. 236.

laid down, as shown upon a larger scale in fig. 236, which represents only one fourth the area of the bed, in such a way as to form channels for the access of air beneath the heap, and a wooden shaft (c) is built up in the centre; the larger lumps of ore are then spread upon the wood above the opening (*c*) in the form of a conical heap (*d d*), up to the level of the central shaft, and covered over with layers (*f f*) of the dust or smaller fragments of ore, stamped down to prevent access of air. The wood is set fire to below, and the combustion regulated by closing or opening the air channels beneath the wood. A heap

of this kind contains from 100 to 200 tons of ore and remains burning for 20 or 30 weeks. A number of cavities (*ssss*) are formed at the top of the heap which serve for the collection of the sulphur given off from the ore in sufficient amount to cover the cost of roasting. This operation is sometimes repeated once or twice until the ore has been sufficiently oxidised. Ore containing much blende is sometimes lixiviated after the first roasting in order to dissolve out the zinc sulphate formed by the oxidation of that substance.

The smelting of lead ores is conducted either in low furnaces called hearths, in shaft furnaces, or in reverberatory furnaces.

Smelting in Hearths.—By heating lumps of galena in contact with burning fuel part of the lead is reduced to the metallic state and part remains in the state of sulphate. Such a method of smelting could only be applied to very pure ore, and moreover it would involve a very considerable waste; it is, however, practised to some extent, and the rudest form of lead smelting is carried out in this way in the back-woods hearth, represented by fig. 237, and consisting simply of a square chamber in which the ore is heated with wood or other fuel. The metal, reduced partly by the two reactions above described and partly by the action of the carbonaceous substance of the fuel upon the lead sulphate, runs out through the arched opening on one side of the chamber into a pit made for its reception, and through the same opening atmospheric air is supplied for the combustion of the fuel. The ancient British smelting furnaces used in Derbyshire were probably of this nature, and prior to the introduction of bellows worked by water power, they were placed in such a position as to be exposed to the prevailing wind. At the present day an artificial blast of air is always used.

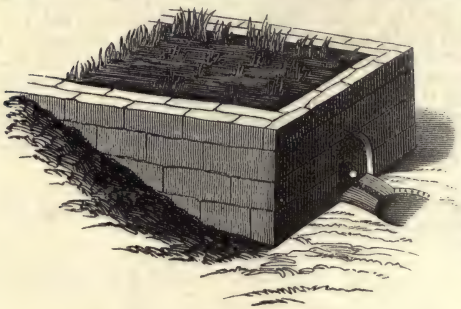


Fig. 237.

The simplest form of blast furnace is that known by the name of the ore hearth, in which the ore is reduced by heating it in contact with fuel. One form of this furnace, called the Scotch ore hearth, is much used in Scotland and the northern parts of the country; a somewhat similar furnace is used in America.

The Scotch ore hearth is represented in vertical section by fig. 238. It consists of a rectangular chamber (c) about 22 inches square and 2 feet high, built of refractory material or lined with cast-iron plates. At the front of the furnace is the sloping work stone (m), over which the reduced lead flows out of the furnace, and beyond it is a cast-iron pot (p) to receive the metal. The bellows' pipe is placed in a cavity at the back of the hearth, about 6 inches above the level of the work stone.

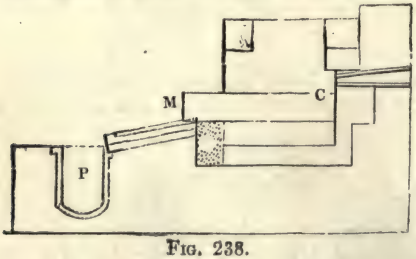


Fig. 238.

The ore can be worked in the hearth either raw or calcined, but it is now usual to calcine it previously; it is placed upon the surface of the burning fuel in the hearth bottom, and when submitted to the action of the blast for about five minutes it melts and is reduced, running down between the fuel into the hearth bottom. Fresh portions of ore are added in this way at intervals until the hearth becomes filled with lead upon which floats a mass of burning fuel mixed with partially melted and reduced ore, which is termed browse. From time to time a poker is thrust into the hearth so as to raise up and open the mass as well as to bring some portion forward upon the work stone to make room for fresh supplies of ore. The browse thus brought forward is then examined, any lumps that have been formed are broken up, and those which have become vitrified or hardened by the heat are picked out for working by another method. Such lumps are called 'grey slag.' A little slaked lime is then sprinkled over on the work stone; if it has a pasty appearance fresh fuel is added, and the browse pushed back into the hearth is covered with a further quantity of fresh ore.

Either peat or wood is used as fuel in this operation, and as it proceeds the reduced lead sinks down into the hearth bottom until it flows over the work stone into the iron pot (P), from which it is transferred by ladles into moulds.

In working the ore hearth the regulation of the blast is an important point. Too weak a blast would not produce sufficient heat for the reduction of the ore, and too strong a blast would cause the production of slag containing lead. The nature of the ore operated upon also requires to be considered.

The ore hearth, when constructed in the manner above described, allows lead fumes to escape; and besides the loss thus occasioned there is a possibility of detriment to the workpeople. In order to obviate this objection the modification represented by fig. 239 has been introduced, the hearth being covered with a brickwork

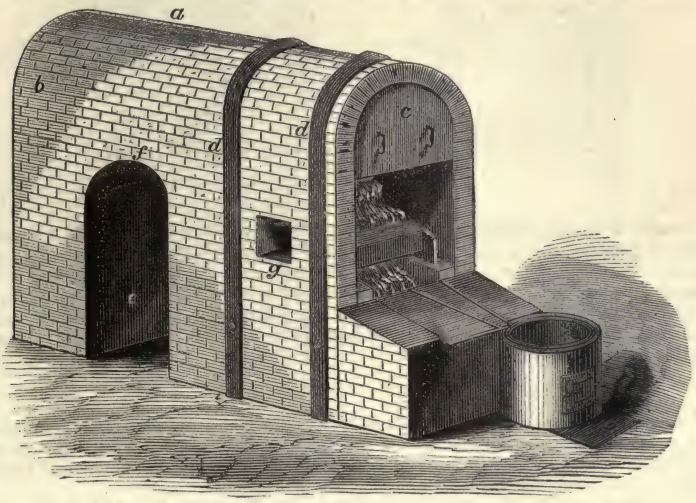


Fig. 239.

hood (*a*), at the back of which there is an opening into the flue, and the area of this opening can be regulated by means of a damper movable from outside at *b*. The opening in front can also be adjusted by the movable iron plate (*c*), which can be raised or lowered as requisite. The brickwork hood is securely bound with iron bands (*d d*), through which bolts pass from side to side of the hood. The opening (*e*) under the arch (*f*) admits of access to the tuyere at the back of the hearth for the regulation of the blast, and the opening (*g*) at the side is for introducing the charges of ore and fuel.

The American ore hearth represented by fig. 240 is constructed with a hollow cast-iron casing (*d*) round the upper part of the hearth (*a*), which serves for heating the

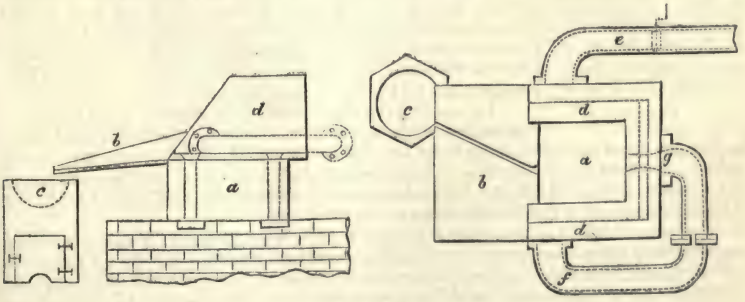


Fig. 240.

air by which the blast is produced, inasmuch as it is forced into the pipe (*e*) and after traversing the hollow casing (*d*) escapes into the hearth through the tuyere (*g*).

The work stone (*b*) is made of cast iron, with a gutter for the melted lead to flow into the iron pot (*c*). The form of the ore hearth is used in Carinthia, and it is worked essentially in the same manner as the Scotch hearth.

In smelting lead ore in these hearths, waste products containing partially reduced lead ores accumulate in course of time under the name of hearth ends, which are generally washed, roasted, and smelted in the same way as fresh ore. The vitrified product known as grey slag contains lead chiefly in an oxidised condition, and it is smelted in the slag hearth described below.

The slag produced in working the ore hearth has been analysed by Plattner and found to have the following composition:

Silica	5·260
Lead oxide	37·710
Sulphuric acid	5·038
Ferric oxide	19·500
Zinc oxide	19·200
Lime	8·856
Magnesia and manganous oxide	1·417
Alumina, cupric oxide, and alkalies	1·760
Molybdic acid	·460
	99·201

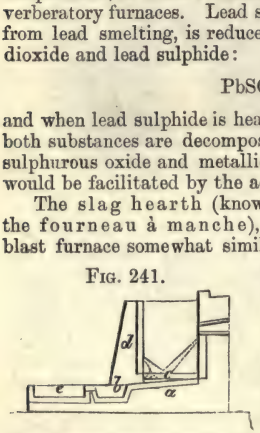
The rich slags resulting from the smelting of lead ore either in hearths or reverberatory furnaces, and containing lead in an oxidised condition, are smelted by a process of reduction; either in contact with the fuel used for producing the requisite temperature, in blast furnaces, or, with the addition of carbonaceous materials, in reverberatory furnaces. Lead sulphate, which is a frequent constituent of the rich slags from lead smelting, is reduced at a red heat by carbon, with formation of carbonic dioxide and lead sulphide:

$$PbSO_4 + 2C = 2CO_2 + PbS;$$

and when lead sulphide is heated to a sufficiently high temperature with lead sulphate, both substances are decomposed in the manner already mentioned, with production of sulphurous oxide and metallic lead. The smelting of slags containing lead silicate would be facilitated by the addition of ferrous silicate.

The slag hearth (known in Germany as the Krummofen, and in France as the fourneau à manche), represented by figs. 241 and 242, is a small rectangular blast furnace somewhat similar to the ore hearth. The sole (*a*) is a cast-iron plate sloping towards the fore hearth (*b*), into which the melted material is discharged. On each side of the sole plate there are strong cast-iron beams (*c c*), called bearers, which support the side walls, and the cast-iron plate (*d*) called the fore stone, which carries the front wall of the shaft, leaving an open space above the sole plate about 7 inches high. The back of the hearth is lined with an iron plate reaching up to the tuyere, which is about 20 inches above the sole plate. The cistern (*e*) in front of the fore hearth is kept full of water, so that the melted slag flowing off from the surface of the lead in the fore hearth is suddenly cooled and granulated, and thus admits of the more easy separation of the lead mechanically mixed with it. The lead runs off from the fore hearth into an iron pot (*f*) which is kept hot by a fire.

Fig. 241.



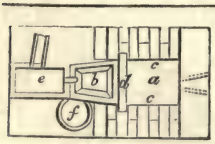


Fig. 242.

In working the slag hearth the bottom is filled with coke or cinders up to within 4 or 5 inches of the tuyere, and when the fire has been got up the slag to be smelted is thrown on, the alternate addition of fuel and the material to be smelted being repeated at intervals. The process is one of reduction, effected chiefly by the carbonaceous portion of the fuel, with production of metallic lead and a fusible slag nearly free from lead.

The loss of lead in smelting by the slag hearth is very great in all cases, but very much depends upon the manner in which the operation is conducted. In all cases the hearth should be covered, not only to protect the workmen from the effects of the fume, but also to reduce the loss of lead by volatilisation, by making the furnace gas pass into a long flue, where the lead is condensed and deposited.

Though the slag hearth, as its name indicates, is specially intended for working up by products which contain too much lead to be thrown away, a modification of it is sometimes used for smelting ores containing only a small amount of lead, which is

chiefly in an oxidised state. In Spain, for instance, ores occur very abundantly consisting of earthy carbonates mixed with lead carbonate, and containing from 5 to 15 per cent. of lead, together with silver amounting to about 15 or 20 ounces per ton, and the smelting of these ores is conducted in furnaces similar to the slag hearth.

The Spanish slag hearth represented by figs. 243, 244, and 245, has been introduced into this country, and is much used for smelting poor and easily fusible slags

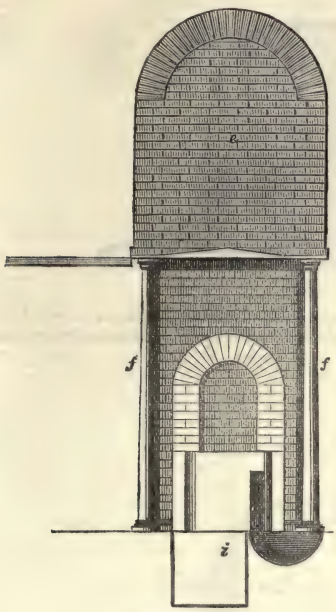


FIG. 243.

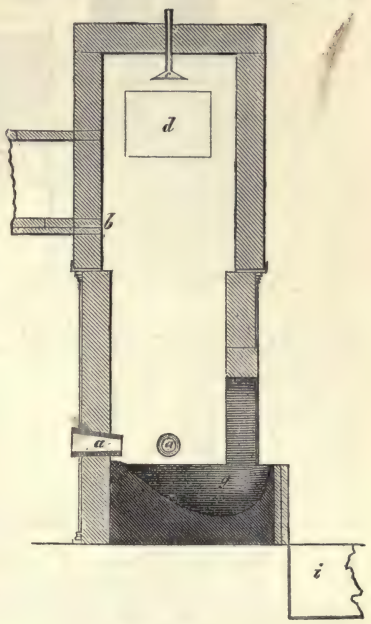


FIG. 244.

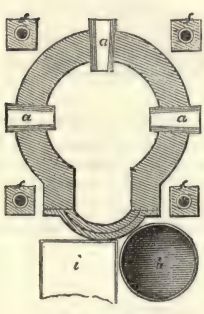


FIG. 245.

containing lead. It consists of a hollow shaft of fire brick, the upper part of which is supported upon four cast-iron pillars (*ffff*), to admit of the body of the furnace being renewed when requisite without interfering with the upper part. The hearth (*g*) is dish-shaped and made of a mixture of coke dust and fire clay. The breast of the furnace is made of a semicircular plate of cast iron, with a lip to carry off the slag and a slot furnished with a clay plug, by withdrawing which the lead accumulating in the hearth is let off into a pot (*h*) at the side of the furnace. There are generally several tuyeres a short distance above the level of the breast plate.

In working this furnace it is charged up to the level of the door (*b*), and the lead fume passes off through the aperture (*d*) into a flue. The lead in the materials smelted exists chiefly in the oxidised state as silicate, etc., and the reducing agent is either metallic iron or slags containing ferrous silicates. Fluor spar is often used as a flux, and when the materials contain barium sulphate it is especially useful. The slag is either allowed to run into the breast pan (*i*) containing water, or into cast-iron waggons, and turned out in blocks when it has solidified.

In Spain a furnace is used for lead smelting, the working part of which resembles the slag hearth in its construction, but the ore is worked without a blast, the draught being produced by a chimney instead, as shown by figs. 246, 247, and 248. The body of the furnace is about 8 feet high, and 4 feet wide. Six openings (*c c*) are left in the walls for the admission of air and for drawing off the slag. The furnace is con-

nected with the chimney (A) by the flue (C), supported on the arch (K). The chimney (A) is about 50 feet high, and has an area large enough to work two furnaces. The

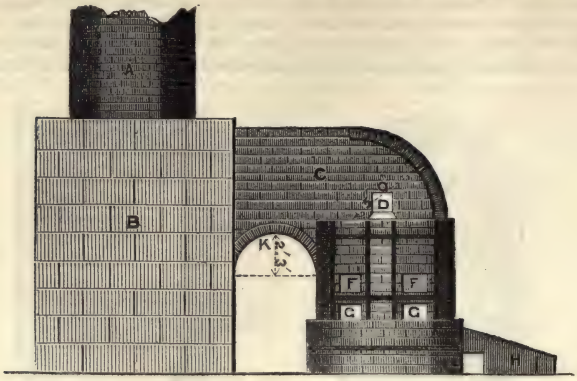


FIG. 246.

air holes (GG) are 12 inches high and 15 inches wide outside, tapering inwards to smaller dimensions, as shown in figs. 247 and 248. Above them are other holes (FF), which

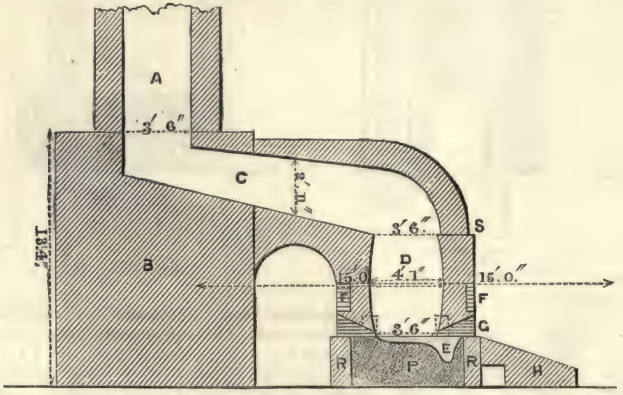


FIG. 247.

are generally bricked up, but can be opened if requisite. The inclined plane (H) serves for raking out the slag, and the door (D) for charging the furnace. In the sectional view of this furnace, fig. 247, the shape of the sole (P) is shown. It is made of a refractory argillaceous material, ground to fine powder with one third its weight of coke, moistened with water, and stamped down into a compact mass. The crucible (E) is then cut out, and in working the furnace the reduced lead collecting in it is run off into a metal pot (T, fig. 248).

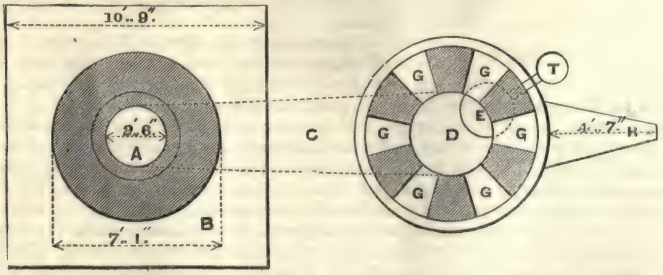


FIG. 248.

Smelting in Shaft Furnaces.—Lead ores containing earthy admixtures in considerable amount are advantageously smelted in shaft furnaces, together with materials suitable for acting as fluxes upon the foreign substances in the ore, and converting them into a sufficiently fusible slag. The decomposition of the sulphide or other lead compounds may be in this case effected by metallic scrap iron added to the charge, or by ferruginous materials which are capable of yielding iron when heated in contact with carbon. The ferrous sulphide formed in this way by the combination of the reduced iron with the sulphur of the galena does not mix with the metallic lead separated, neither is it dissolved by the slag, and when the melted contents of the furnace are run out, it separates as a distinct layer between the reduced metal and the slag, forming what is termed *regulus* or *matt*. In smelting lead ores by means of iron, part of the lead contained in the ore is almost always retained in the regulus by the combination of the ferrous sulphide with some of the lead sulphide, and consequently further operations are necessary for obtaining the whole of the lead, or there is a loss of this metal proportionate to the amount of regulus produced.

The proportion of lead retained in the regulus is to a great extent dependent upon the temperature. The higher the temperature the more completely is the lead sulphide decomposed, and hence, so far as the yield of lead is concerned, the use of coke as fuel has given better results than wood. However, this method of smelting has not been found advantageous when the ores worked are rich in galena, and do not contain copper; in which case it is desirable to avoid the production of regulus.

One of the chief advantages resulting from the use of iron in smelting poor sulphuretted lead ores consists in the separation of any copper they may contain; since the sulphide of this metal is less readily decomposed by iron than the lead sulphide associated with it, and as it combines more readily with ferrous sulphide, the greater part of the copper in the ore is retained in the regulus formed. In the case of argentiferous lead ore, the greater part of the silver is obtained in the metallic lead and a smaller proportion is retained in the regulus; but, in order to secure this result with the greatest advantage, it is requisite that the proportion of silver to lead in the charge should not be too great, and since silver sulphide combines readily with ferrous sulphide, it is often necessary in smelting ores rich in silver to limit the amount of silver in the regulus, by smelting the ore in such a manner that a large proportion of the lead remains in the regulus. In some cases it is even necessary to add metallic lead to the materials smelted in order to prevent the retention of too much silver in the regulus.

Among the other minerals associated with galena in mixed ores blende is to some extent dissolved in the slag; part of it is decomposed by metallic iron, and the zinc volatilised gives rise to the formation of deposits in the upper part of the furnace, where it comes into contact with atmospheric air. The sulphur compounds of arsenic and antimony are also decomposed by iron, and the metals are either volatilised, or they combine with iron, copper, nickel, and cobalt, forming the product known as speise. Some portions of the zinc, antimony, and arsenic are retained by the lead and by the regulus, and part of the antimony in an oxidised state is taken up by the slag.

The substitution of slags consisting of ferrous silicate in the place of metallic iron for smelting sulphuretted lead ores is no doubt, to some extent, an economical plan of supplying iron for the decomposition of the lead sulphide in the ore; but it is also probable that there is a more direct reaction between the lead sulphide and part of the ferrous oxide of the silicate, resulting in the formation of ferrous sulphide and lead oxide, which again reacts with a further portion of the lead sulphide, forming sulphurous oxide and metallic lead. The final effect of these reactions may be represented by the following equation:

$2(2FeO,SiO_2)$	+	$5PbS$	=	$3Pb$	+	$2(FeS,PbS)$	+	$2(FeO,SiO_2)$	+	SO_2
408		1195		621		654		264		64

Ores containing a large proportion of pyrites or other sulphides besides galena would yield a large quantity of regulus when smelted with iron, and in order to avoid this result, as well as to economise iron, and to obtain lead free from arsenic or antimony, such ores are roasted sufficiently to oxidise the excess of sulphides, and to volatilise some of the impurities. These ores are sometimes roasted to such an extent as to oxidise the lead as well as the other metals, and then smelted in shaft furnaces with slag capable of dissolving the metallic oxides, which are not so readily reduced as the lead oxide by contact with carbonaceous gases at a high temperature. Even in this case a certain amount of regulus is always formed, since the sulphates produced to some extent by roasting lead ores containing sulphides are deoxidised in the smelting, and again converted into sulphides. In smelting according to this plan some lead is also reduced by the reaction of oxygenated compounds with lead sulphide.

Very poor lead ores containing argentiferous minerals and small quantities of

copper pyrites, etc. are sometimes smelted together with fluxes and iron pyrites sufficient to separate the whole of the lead, silver, and copper in the regulus, which is afterwards roasted and smelted in the same manner as a roasted lead ore.

The furnaces employed in smelting lead ores by these methods differ from the slag hearths chiefly in having the lateral walls carried up to a much greater height, so that they contain a considerable quantity of the material to be smelted, as a column extending several feet above the level of the tuyere. The charge is therefore subjected for some length of time to the action of reducing gases in the upper part of the shaft, and is gradually heated to a temperature at which the various substances contained in it are decomposed by heat, or by the action of reducing gases, or by reacting upon each other. Owing to the solubility of lead and its sulphide there is always a considerable portion of the metal carried off in the current of gas escaping from the throat of the furnace, and on this account it is generally connected with a long flue or a series of chambers in which the volatilised lead is gradually deposited.

In Silesia a furnace is used of the form represented by fig. 249. It consists of a brick shaft (*a a*) about 18 feet high, and for some distance above the tuyere (*t*) the section is rectangular, above that height it is circular. The exterior wall (*c c*) is built of ordinary bricks, and the lining (*a a*) is built of fire brick. At the level of the charging door (*f*) is a floor (E), upon which the ore and flux are mixed before being thrown into the furnace; and the fume passes off from the top of the furnace into condensing chambers.

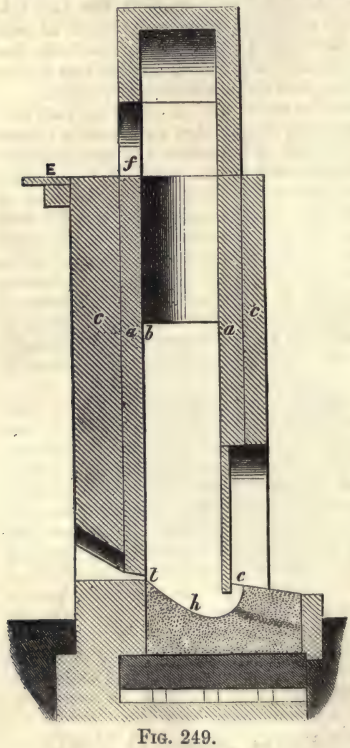


FIG. 249.

In working this furnace it is charged with lead ore or slag, cast iron, and forge slag. The melted products, consisting of metallic lead, regulus and slag, sink down into the hearth and are either run off at the breast (*c*) or by tapping a channel that passes to the bottom of the hearth. The regulus sometimes contains in addition to ferrous sulphide 7 or 8 per cent. of lead in the state of sulphide, and then it is roasted and worked again, but otherwise is thrown on the waste heap. The slag consists chiefly of ferrous silicate, but sometimes it contains sufficient lead to be worked again.

The regulus obtained in this operation at some other works contains as much as 30 per cent. of lead, together with a considerable amount of copper and some silver, and it is worked in various ways according to its composition. For the complete extraction of the lead several smelting operations are sometimes necessary, and the regulus ultimately obtained, containing greater part of the copper, is rich enough in this metal to be worked for copper. Regulus poor in lead is sometimes roasted and lixiviated to extract the soluble sulphates of copper or zinc, and the copper obtained by precipitation with iron. When the amount of iron in the roasted regulus is large, it is again used as a flux in smelting ore.

The lead ores smelted by the iron method in the Upper Hartz contain galena mixed with some copper pyrites, fahl-ore, bournonite and blende. The amount of silver varies considerably, and in some instances the argentiferous galena is accompanied by true silver ores, as well as minerals containing large amounts of copper, nickel, antimony and arsenic. The principal gangue substances are quartz, calcspar and heavy spar.

These ores are smelted both in the state of lumps and as a coarse powder, and they are mixed, according to the nature of the substances constituting the gangue, in such a manner as to give rise to the production of a fusible slag, and so as to contain on the average about 55 or 63 per cent. of lead, in proportion to the amount of silver in the material smelted. Materials containing lead oxide are also added, partly for the sake of extracting the lead they contain and partly to facilitate the extraction of silver from the ore smelted. The separation of the quartz is effected by means of

an addition of slag containing a sufficiently large proportion of ferrous oxide to dissolve the quartz and form a fusible slag, while at the same time it prevents the formation of lead silicate. In some cases the ore contains a considerable amount of blende, and then it is necessary to increase the proportion of basic slag. The slag produced in the smelting of regulus (p. 371) is used for this purpose, as it always contains some lead which augments the yield from the ore.

The shaft furnace used at Clausthal in the Harz, represented by figs. 250 and 251, is about 24 feet in height from the breast to the charging door (T), and the upper part communicates with a series of condensation chambers (c c). The tuyere is 18 inches above the sole; and the hearth, projecting beyond the breast (*b*) of the furnace, slopes at the bottom from the back to the front. The slag flows out at the breast, and as it solidifies it is drawn down the incline (*p*). At the side is an iron pot (*a*) to receive the melted lead when the tap hole leading to the bottom of the hearth is opened.

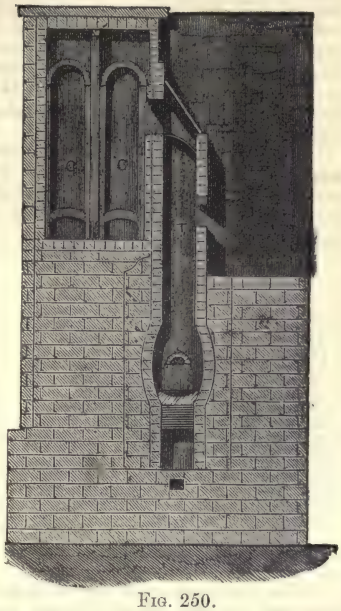


Fig. 250.

The hearth is formed of refractory sandstone, and is lined with a mixture of clay and charcoal stamped down to form a hollow space or crucible, in which the melted products of the operation collect and separate in layers before escaping from the furnace.

In charging this furnace the ore is always thrown towards the back against the tuyere and the fuel towards the breast of the furnace; by this means a channel or nose of solidified slag, about 8 or 10 inches long, is formed opposite the tuyere, and the successful working of the furnace depends very much upon the way this is managed.

As a result of this method of charging, the mixture of ore, slag, etc. to be smelted forms a vertical layer above the nose of the tuyere, and the blast passing through the nose impinges directly upon the fuel, which forms a similar layer against the front of the furnace. The highest temperature is therefore at the centre of the furnace, near the level of the tuyere. When coke is used as fuel, there is greater difficulty in regulating the operation, as the furnace is liable to become too hot; but it has nevertheless been substituted almost entirely for charcoal. The throat of the furnace is not allowed to become red hot, in order to prevent the oxidation of the iron, and to limit as much as possible the loss of lead as fume and dust.

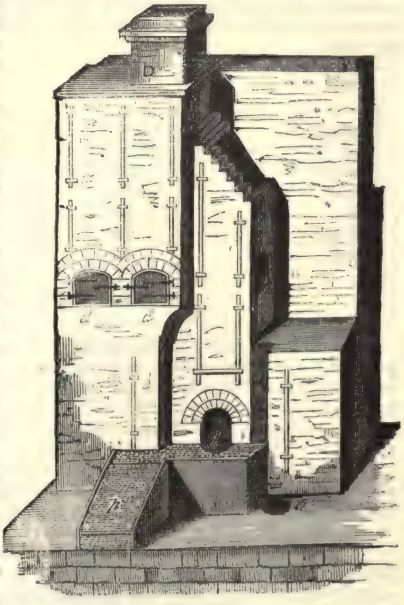


Fig. 251.

The charge, consisting of finely-divided ore, old hearth bottoms, or other materials containing lead oxide, together with granulated cast iron, and a quantity of slag from previous operations, is gradually heated in the upper part of the shaft, and the lead oxide contained in it is probably to some extent reduced by the ascending current of gas; but the reaction between the iron and lead sulphide does not take place until the materials of the charge have sunk down to a point near the tuyere, and before reaching the level

B B

of the tuyere this reaction should be complete. It is at this part of the shaft also that the combination of silica and other gangue constituents with the ferruginous slag takes place, and the melted products of these reactions, sinking into the hearth, separate according to their density, but do not undergo much further change. The higher the temperature of the furnace at the point where the reaction of the iron and lead sulphide takes place, the more complete is the decomposition of the lead sulphide, and the smaller the proportion of lead retained by the regulus produced; but at the same time there is a greater risk of loss from volatilisation of lead, unless the furnace be provided with ample means of condensation. Since the greater part of the lead in the materials smelted is in the state of sulphide, there is less risk of loss by the formation of lead silicate and the production of slag containing lead than there is in smelting roasted ores.

The products of the operation consist of metallic lead containing silver, regulus, or a mixture of ferrous sulphide with lead sulphide and cuprous sulphide, also containing some silver, and a black glassy slag consisting chiefly of ferrous silicate, the composition of which approximates to the formula FeO,SiO_2, as shown by the following analyses:

	Bodemann	Rammelsberg
Silica	48·80	45·00
Alumina	4·62	4·62
Ferrous oxide	36·00	35·83
Lime	3·26	6·31
Magnesia	1·24	0·75
Lead oxide	5·30	7·80
Antimonous oxide	—	0·50
	99·22	100·81

The lead obtained contains from 0·1 to 0·2 per cent. of silver, from 0·4 to 0·76 per cent. of copper, 0·2 to 3·46 per cent. of antimony, sometimes with traces of iron, zinc, and sulphur.

This lead matt or regulus is frequently crystalline; it has a bluish grey colour somewhat like that of lead and iron, and soon becomes tarnished by superficial oxidation of the ferrous sulphide, and then it presents the colour of magnetic pyrites; it contains a considerable amount of metallic lead disseminated through it in a very minute state of division, and has a very variable composition, as shown by the following table:

	Brüel		Bodemann			Joy
Sulphur	15·34	16·40	17·27	18·92	19·33	16·12
Lead	73·35	60·69	65·78	59·33	53·31	52·27
Iron	9·90	20·55	13·15	19·79	21·77	28·32
Copper	0·39	0·49	1·15	1·10	0·23	1·42
Zinc	·20	0·55	0·67	0·17	2·25	1·56
Antimony	·40	·36	0·18	0·13	0·38	0·31
Silver	·12	·11	—	—	—	—
	99·70	99·15	98·20	99·44	97·27	100·00

On account partly of the presence of metallic lead in this regulus, the relative proportions of sulphur lead and iron deviate from that of the double iron and lead sulphide, FeS + PbS, which contains 19·57 per cent. of sulphur, 63·33 per cent. of lead, and 17·10 per cent. of iron. However, it is probable that this compound constitutes the greater part of the regulus, together with varying amounts of copper, antimony, zinc, silver, etc., in the state of sulphides.

In order to extract the lead retained in the regulus or matt, it is first roasted so as to separate the greater part of the sulphur as sulphurous oxide and ultimately convert the metals into the state of oxides. A considerable portion of the lead sulphide is left in the state of sulphate, when the amount of lead in the regulus is large.

The roasting of this regulus is conducted in heaps under sheds, and it gradually becomes bluish-grey, earthy, and friable. It is then smelted with cast-iron, materials containing lead oxide and some silicious slag from previous operations in a slag hearth, the construction of which is represented by figs. 252, 253, and 254. The shaft (A B) is about 4 feet 6 inches high, and wider above than below.

Coke is used as fuel; and during the melting, part of the iron in the oxidised regulus combines with the silica of the slag, forming a more fusible silicate, and the lead sulphide is reduced either by the oxidised materials or by the metallic iron, yielding metallic lead and another regulus. The carbon of the fuel also helps the reduction of lead. In this way, by repeating the operations of roasting and smelting several times, the amount of lead in the regulus is reduced; and in the last melting, when the addition of materials containing lead oxide is omitted, a regulus is obtained with very little lead, but almost all the copper that was contained in the original ore.

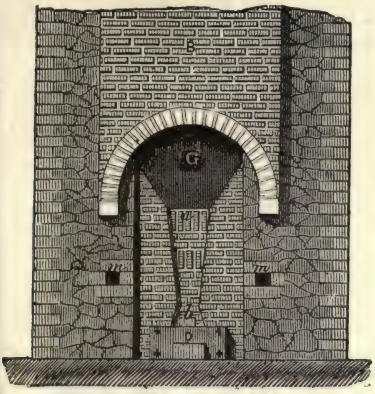


Fig. 252.

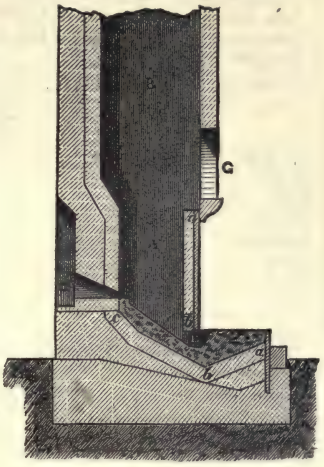


Fig. 253.

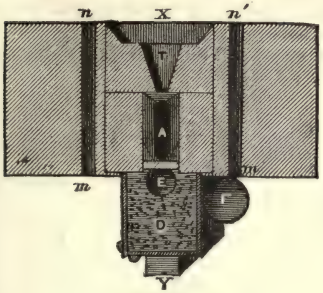


Fig. 254.

The furnace is worked with a single tuyere (T) placed at the back; the sole slopes sharply downwards from the level of the tuyere, and the lowest point extends beyond the breast of the furnace, forming a crucible (E) in which the melted materials collect and are drawn off at intervals by tapping into the receptacle (F) outside, fig. 254 representing a horizontal section at the level of the tuyere, and fig. 253 a vertical section; from X to Y show the mode in which the sole and crucible are formed, charcoal and clay stamped down upon the slabs of stone (*a*, *b*, *c*) at the bottom of the furnace.

The composition of the slag obtained in smelting the lead regulus is shown by the following analyses:

	Rammelsberg	Bodemann	Kerl	
Silica	39·79	32·34	29·90	37·79
Ferrous oxide	46·44	43·90	33·60	46·44
Lead oxide	9·17	10·01	2·34	21·56
Lime	2·12	2·07	2·07	13·63
Alumina	traces	5·06	3·12	9·98
Ferrous sulphide	,,	3·50	—	—
Manganous oxide	—	1·20	—	—
Cupric oxide	—	·05	—	—
Potash	—	·05	—	—
	97·52	98·18	—	—

The last two columns of the table give the maximum and minimum amounts of the several constituents of the slag obtained in smelting the lead regulus. A comparison with the table at p. 370 will show that this slag is much more basic than that pro-

duced in smelting the ores, in consequence of its having dissolved part of the ferrous oxide formed in the smelting of the roasted regulus.

The lead obtained by smelting regulus contains a larger amount of copper and antimony than that obtained in smelting the original ore, but at the same time the greater part of the copper in the materials operated upon is retained in the regulus that is obtained in each successive smelting together with metallic lead, unless the roasting of the regulus has been carried too far, and too much iron has been used in smelting it, in which case some copper would pass into the slag, and the lead obtained would also contain too much copper.

The following analyses show the effect of the operation in augmenting the relative proportions of copper to lead in the regulus, until at last it presents the composition of a copper regulus:—

	No. 3 regulus Brüel	No. 4 regulus Bodemann
Sulphur	17·12	15·55
Lead	43·07	32·07
Iron	8.03	13·15
Copper	30·46	34·01
Antimony	0·74	2·67
Silver	0·12	0·07
	99·54	97·51

The further treatment of such regulus for the extraction of the copper will be described under the head of 'Copper Smelting.'

Lead ores containing arsenic, antimony, nickel, and cobalt, yield in smelting a peculiar product called speise, which separates as a distinct layer in the hearth, between the metallic lead and the regulus: it has a steel-grey colour generally, but is sometimes almost as white as silver. The fracture has a metallic lustre, and is granular or laminated, like specular pig iron; it is brittle, magnetic, and has a specific gravity of 7·381. The composition is shown by the following analyses:—

	Jordan	Ahrend	Rammelsberg
Sulphur	7·82	2·86	2·04
Arsenic	5·05	12·98	29·13
Antimony	3·35	5·21	
Iron	68·03	5·54	51·74
Copper	5·68	44·56	3·55
Nickel	6·52	0·71	8·85
Cobalt	1·67	1·63	2·89
Lead	0·60	26·11	trace
Silver	·003	·13	—
	98·723	99·73	98·20

These products consist essentially of arsenides and antimonides mixed with sulphides. Speise of this kind is always produced to some extent at the Lower Hartz lead works.

Formerly the lead speise was repeatedly roasted and melted, in order to concentrate the cobalt. More recently, it has been the practice to melt it with wood under a blast, so as to obtain black copper containing cobalt and nickel, together with a greenish-black slag, which finally becomes red, and contains about 2 per cent. cobalt with twice as much nickel. (See Nickel and Cobalt.)

The lead ores smelted in the neighbourhood of Goslar in the Lower Hartz contain only a small amount of galena together with iron pyrites, copper pyrites, blende, arsenical pyrites, and antimonial compounds. The gangue substance consists of heavy spar, calc spar, quartz, and schist, so that the amount of lead in the ore is not more than from 4 to 10 per cent. On account of the large proportion of foreign admixtures these ores are roasted before being smelted, and by this means the arsenic, antimony, zinc, and sulphur are partly volatilised. Sulphates are at the same time formed, and by the reduction they undergo in the smelting of the ore there is always a considerable production of regulus. The amount of lead in the regulus is sometimes as much as 20 per cent. The large proportion of zinc in these ores gives rise to the

formation of deposits in the upper part of the furnace, and it is sometimes so considerable that metallic zinc is obtained as a by-product of the smelting operation. Ores containing a very large amount of zinc are sometimes lixiviated after the first roasting to remove the zinc sulphate.

On account of the large amount of metallic oxides in the roasted ores it is necessary in the smelting to use silicious fluxes, in order to dissolve the basic oxides and prevent the formation of deposits in the hearth, in consequence of the reduction of iron and copper. Another reason for adding a sufficient proportion of silica is that slag containing too much basic oxide solidifies rapidly and is so dense that it does not separate readily from the regulus, thus causing considerable loss. Too large a proportion of silica, on the contrary, is disadvantageous, since it promotes the formation of lead silicate, which dissolves in the slag and causes loss of lead.

In the lead works near Goslar the silicious ore slags produced in the Upper Hartz district (p. 370) are used as fluxes, together with waste materials containing lead oxide.

In smelting lead ores by this method lead is produced partly by the reaction of oxidised materials and lead sulphide, partly also by the action of metallic iron upon lead sulphide. The regulus obtained amounts to as much or even more than the lead. It is roasted and smelted again several times in succession, until the lead is sufficiently separated from the copper, and the copper regulus finally obtained is then worked in the same manner as the copper regulus above referred to.

The slags produced in copper smelting, and consisting of ferrous silicate with traces of copper and silver, have recently been employed as the source of iron for the decomposition of lead ores containing galena. The furnace used for this purpose is elliptical, with six tuyeres on each side and a tap hole at each end. It bears the name of the inventor Rachette. The copper slag used in ore smelting has the following composition :—

	Streng	
Silica	17·17	16·95
Alumina	2·73	3·69
Ferrous oxide	69·84	70·27
Lime	3·27	3·37
Magnesia	0·83	1·30
Cupric oxide	1·77	1·90
Manganous oxide	0·54	0·07
Zinc oxide, Cobalt oxide	1·54	0·98
Sulphur	1·58	1·73
	99·27	100·26

This furnace has been tried for some time at the Harz lead works, both by using the cast iron obtained by smelting the copper slags separately and by smelting the lead ore with the copper slags. The lead obtained in this was not more impure than that from the ordinary shaft furnaces, and both the regulus and the slag produced at the same time contained very much less lead than those from the old form of furnace, as will be seen by the following analyses :—

	Regulus			Slag	
	Hilgenberg	Ey		Kerl	Hilgenberg
Sulphur	24·43	26·67	Silica	45·10	41·06
Iron	40·69	55·90	Alumina	8·40	7·28
Lead	29·15	10·88	Ferrous oxide	33·40	38·37
Copper	3·71	3·33	Lead oxide	1·02	0·88
Zinc, Manganese	1·41	1·13	Lime	7·80	7·58
			Magnesia	·90	·93
Antimony, Arsenic	0·13	0·27	Zinc oxide, Manganous oxide	3·40	1·60
			Copper and antimony	traces	traces
	99·52	98·18		100·02	97·70

At Pontgibaud in France the lead ore smelted is a highly argentiferous galena containing admixtures of blende, pyrites, quartz, heavy spar, and felspar. The average amount of lead in the ore is from 25 to 36 per cent. The ore is thoroughly roasted on the upper hearth (*a*) of a reverberatory furnace, figs. 255 and 257, and when com-

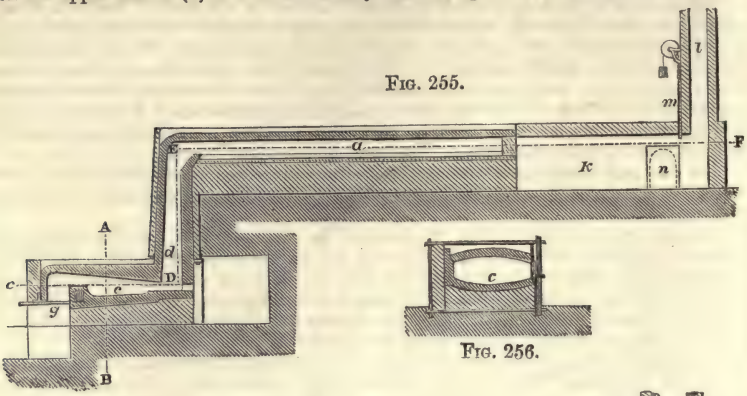


Fig. 255.

Fig. 256.

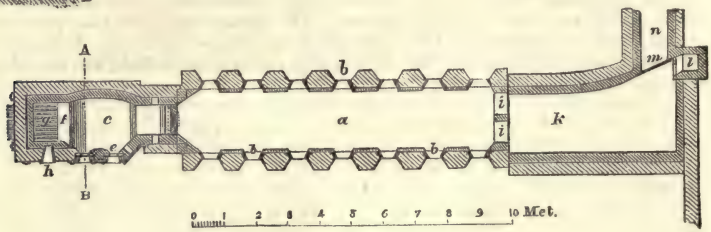


Fig. 257.

pletely oxidised it is transferred through the flue (*d*) to the lower hearth (*c*), where it is sufficiently heated to make the mass melt before it is drawn out. This lower hearth is concave, as shown in fig. 256, which represents a transverse section on the line A B of figs. 255 and 257. Part of the sulphates formed in the roasting are thus decomposed, and the sulphuric oxide driven off passes, together with gaseous products of combustion, through the outlet (*i i*) at the end of the hearth into the condensation chamber (*k*). This chamber is connected with the chimney (*l*) and with a flue (*n*), through which the gas can be passed for the condensation of fume if requisite. In this state the material contains about one-third its weight of gangue substance, consisting chiefly of quartz, felspar, and heavy spar, with about 35 to 40 per cent. of lead, partly in the state of silicate, sulphate, and oxide, with not more than 1·5 per cent. of lead sulphide.

The smelting of the roasted ore is carried out in low shaft furnaces, about 5 feet high, with the addition of metallic iron, fluor spar, limestone, materials containing lead oxide, and slags from previous operations. The products obtained are metallic lead, containing from 0·35 to 0·5 per cent. of silver, and a slag which does not contain more than 3 per cent. of lead when the furnace works well. Sometimes a regulus is produced which contains a large amount of lead, but this is due to defective working; its composition is shown in the following table:—

	Rivot		Berthier
Sulphur	2·3	4·0	23·6
Lead	79·5	67 0	5·
Iron	12·2	22·4	54·6
Zinc	1·1	1·1	—
Arsenic Antimony	4·2	4·5	16·6
	99·3	99·	99·8

The reduction of lead in this case is chiefly due to the action of metallic iron and carbon upon the lead silicate, and the ferrous oxide thus produced combines with the silica, forming a fusible slag. The lead sulphate is probably reduced by reaction with lead oxide, rather than by the iron, when the operation is well conducted, and owing to the small amount of sulphides in the material smelted very little regulus is then produced.

The following analyses of the slags formerly produced at these works will show that the operation was very defective:—

	Berthier	Rivot		
Silica	27·	39·	40·	38·
Alumina	7·6	1·5	1·7	1·4
Ferrous oxide	32·	21·2	18·7	19·2
Lime	13·	11·	15·	24·1
Baryta	—	26·	3·2	3·3
Magnesia	—	2·1	3·2	2·9
Lead oxide	18·6	18·2	13·1	6·0
Zinc oxide	—	1·7	1·5	1·6
Sulphuric acid	—	1·0	2·3	2·1
	—	—	98·7	98·6

At Freiberg lead ores consisting of argentiferous galena, and containing from 20 to 30 per cent. of lead, are smelted with the twofold object of obtaining the lead from them and of making it serve at the same time to extract silver from other ores which contain little or no lead, but consist chiefly of quartz containing argentiferous iron pyrites, copper pyrites, and blende. For this purpose the several ores are mixed so that the average amount of lead is from 20 to 35 per cent. and roasted in order to oxidise the pyritic minerals, as well as to volatilise arsenic, antimony, and zinc. Some of the Freiberg ores which contain too little lead to be worth smelting for this metal alone, but contain a considerable amount of silver and some copper, are smelted together with slags produced in smelting lead ores, so as to obtain the metallic sulphides they contain in the state of a regulus, which is roasted and mixed with the lead ores when they are smelted, with the object of furnishing in the furnace ferrous oxide to combine with the silica of the ores and form a fusible slag. Formerly such poor pyritic ores were smelted in shaft furnaces, but recently these have been superseded by reverberatory furnaces, and the ores are worked together with lead slags containing a small amount of lead, which is by this means extracted, and passes into the regulus together with the silver, lead and copper of the ores. The composition of the regulus is given in the following table:

	Plattner	Richter	
Sulphur	26·49	23·43	21·81
Lead	8·86	7·35	5·69
Iron	57·33	53·81	51·33
Copper	3·27	3·87	11·33
Zinc	1·38	7·65	2·14
Silver	·15	—	—
Nickel	·51	—	—
Antimony	·19	0·84	0·73
Arsenic	1·24		
Silica	—	2·11	—
Oxygen slags	—	—	6·97
	99·42	99·06	100·

Owing to the large amount of pyrites in these poor ores and to the circumstance of their being smelted in the raw state, no metallic lead is obtained, and the effect of the operation consists chiefly in the concentration of such small amounts of lead and copper as the ore contains, while, at the same time, the lead regulus left in the slag produced in smelting the richer ore is extracted.

The slag produced at the same time consists chiefly of ferrous silicate containing about 1 per cent. of lead, 0·24 per cent. copper, and a trace of silver: it is cast into blocks, which are either used at once for building purposes or thrown away.

The richer lead ores are smelted in a shaft furnace of the kind represented by figs. 258 to 261. It is constructed of substantial stone walls (*d e g*) lined with fire brick (*f*) and upon a solid foundation (*c*) under which there are drains (*a b*) to carry off water. Below the hearth there is a bed of slag (*o*) covered by a layer of loam (*p*). The shaft

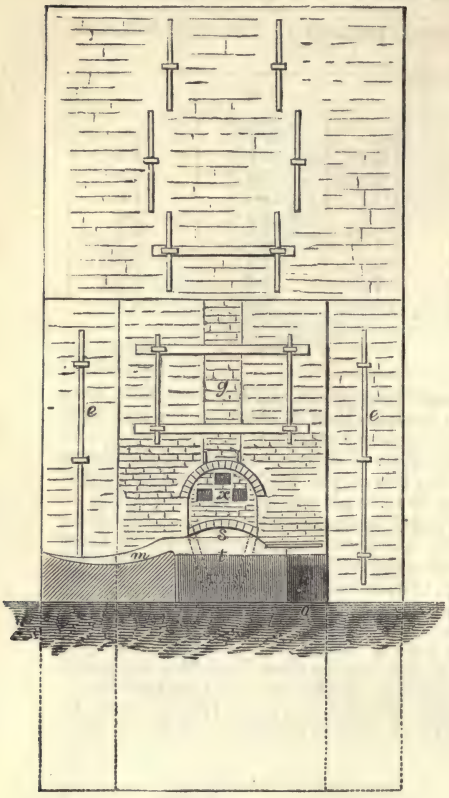


Fig. 258.

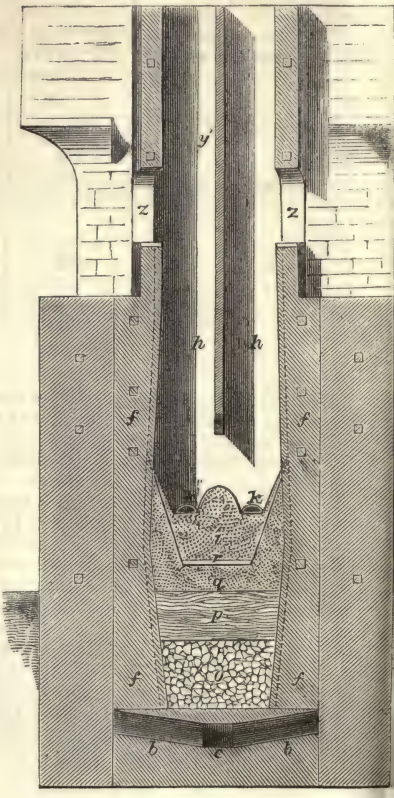


Fig. 259.

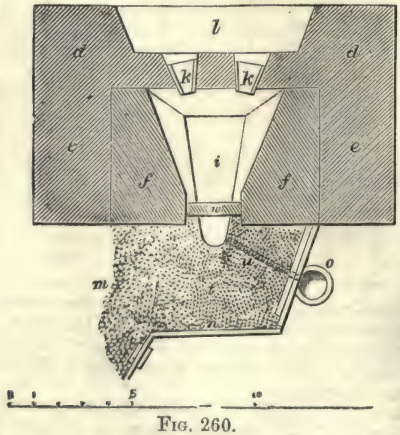


Fig. 260.

is separated by a partition into two parts, and is triangular in section, as shown by fig. 260. The hearth (*i*) projects beyond the breast (*w*) under which the slag flows off into the gutter (*m*) and it is formed of a layer of coke dust and fire clay (*q*) supported in front by the dam plate (*n*). There are two tuyeres (*k k*) set at an angle, and inclined downwards. The charge is thrown in through the doors (*z z*); the holes (*x*) are for removing any obstruction while the furnace is in operation.

In smelting the roasted lead ore it is mixed with roasted regulus from previous operations, fluor spar, lime, and silicious slag. Coke is used as fuel, and the smelting operation is conducted so that a nose is formed before the tuyere and without flame at the tunnel head of the furnace.

The products are metallic lead, regulus, and slag; sometimes, also, a speise con-

sisting principally of iron and arsenic. The lead thus obtained contains about ·5 per

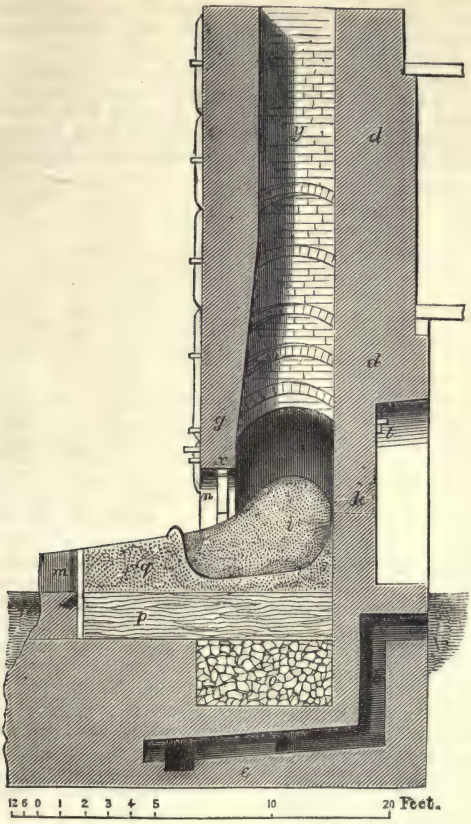


FIG. 261.

cent. silver, together with some copper, antimony, arsenic, and iron, amounting in all to about 3 per cent. of the metal obtained.

The slag produced has the composition given in the following table:

	Plattner		Richter	
Silica	35·16	43·26	28·14	27 05
Alumina	1·06	3·20	5·78	6·85
Ferrous oxide	38·25	33·15	37·23	41·21
Lime	5·96	5·41	7·68	8·84
Baryta	—	—	3·87	—
Magnesia	—	0·71	0·63	0·90
Lead oxide	7·11	5·64	7·35	3·90
Zinc oxide	8·06	7·83	7·60	8·62
Cupric oxide	0·73	0·61	0·50	1·00
Sulphur	3·30	0·32	2·47	3·53
	99·63	100·13	101·25	101·90

The slag as usual contains some regulus mechanically disseminated through the mass, and about 5 or 6 per cent. of lead, with 0·02 per cent. of silver. It is therefore smelted together with the poor ores above mentioned in the reverberatory furnace,

and while the ferrous oxide it contains serves as a flux for the silicious ingredients of those ores, the lead and silver it contains are extracted and obtained in the regulus.

The regulus produced in smelting the lead ore in the shaft furnace amounts to about half the weight of the lead obtained with it, and on the average it contains 20 per cent. of lead, 20 per cent. of copper, and 0·2 per cent. of silver.

The regulus from the blast furnace, after having been roasted, is submitted to a second smelting with slag and various by-products containing lead, by which a further quantity of metallic lead is obtained from it, together with a smaller quantity of regulus containing some of the lead, the composition of which is shown by the following analyses, 2, 3, 4, as compared with the composition of the first regulus 1 :

	1	Plattner		
		2	3	4
Sulphur	19·53	21·31	19·85	22·85
Lead	25·13	20·25	23·29	21·82
Iron	33·12	27·05	36·02	37·20
Copper	12·10	27·61	15·28	12·94
Nickel	—	1·01	2·33	·54
Zinc	—	0·23	0·14	1·44
Silver	·20	0·12	0·12	0·10
Arsenic	2·45	0·65	1·25	0·73
Antimony	4·75	1·00	0·85	·72
Carbon	—	—	—	—
	—	99·23	99·13	98·34

It is probable that part of the lead in this regulus is in the metallic state, being dissolved by the melted ferrous sulphide of which it chiefly consists. From the foregoing figures it will be seen that in the regulus from the ore smelting the proportion of copper to iron and lead is much smaller than it is in the regulus obtained by the subsequent operation of smelting the first regulus from the shaft furnace with materials containing lead oxide. The effect of this operation is in fact not only to separate lead in the metallic state, but also to concentrate the copper in the regulus.

The subsequent treatment of the regulus is intended to effect a further separation of the lead and silver from the copper; for this purpose the regulus is slightly roasted in kilns so as to convert the greater part of the iron and lead into the state of oxides, while leaving the copper as sulphide. It is then smelted together with blast-furnace slag, which is sufficiently silicious to dissolve the oxidised iron. The products of this operation are metallic lead containing most of the silver and some copper, together with copper regulus, containing lead and some silver, in the proportions shown by the following analysis, and a slag consisting of ferrous silicate :

Copper Regulus.

Sulphur	21·00
Copper	36·20
Lead	24·80
Silver	0·16
Arsenic	—
Iron	15·20
Nickel } Zinc }	2·64
	100·00

Copper Regulus Slag.

	Brooks
Silica	28·05
Ferrous oxide	61·08
Alumina	4·33
Lime	3·02
Magnesia	0·85
Lead oxide	2·67
Cupric oxide	trace
	100·00

The slag from this operation is used as a flux in smelting silicious ores, or in smelting regulus, and according to the amounts of lead and silver in the copper regulus it is either roasted and smelted again with materials containing lead oxide, until a regulus is obtained containing 50 or 60 per cent. of copper with about 10 per cent. of copper, or treated at once for copper. (See Copper Smelting).

Smelting in Reverberatory Furnaces.—In the extraction of lead from galena by this method, the ore is in the first instance partially roasted, so as to convert some of the sulphide into lead sulphate and lead oxide (see p. 360); the heat is then raised to such a degree that these substances react upon the unaltered portion of sulphide, yielding in both cases metallic lead and sulphuric oxide, according to the following equations: $PbS + PSO_4 = 2Pb + 2SO_2$, and $PS + 2PbO = 3Pb + SO$

In order to obtain this result in the most advantageous manner, it is evident that the roasting operation must be regulated so as to furnish lead oxide and sulphate in such proportion relatively to the unaltered sulphide as is indicated by the foregoing equations. An essential condition of this method of smelting sulphuretted lead ores is that they should consist chiefly, if not entirely, of galena. Ores containing admixtures of other sulphides, oxides, etc., are not so advantageously worked by this method (see p. 384), and the presence of silica or silicates is very prejudicial on account of the liability to the formation of fusible lead silicate which does not react with lead sulphide in the same manner as the sulphate does, and mixing with the slag causes very great loss. The lead ore is therefore carefully prepared so as to separate quartz and other substances from the galena, but since the purification of the galena by such preparatory operations is never complete, the slag produced in smelting lead by this method always contains some lead, and very frequently sufficient to admit of being worked by other methods for the extraction of the metal. Even when pure galena is operated upon in the reverberatory furnace, a certain amount of the lead remains in the slag.

The reverberatory furnace employed in lead smelting is somewhat differently constructed in different localities, and the hearth is either cup-shaped with the lowest point at the centre, or it is uniformly inclined towards the end of the furnace, and is slightly hollowed in the same direction at the slope. The former mode of construction is designed for melting down the charge in one mass, and retaining it in a melted condition long enough to allow the separation of the reduced metal from the slag, and furnaces of this kind are chiefly used in England, Brittany, and Savoy. The furnaces with sloping hearth are used in Carinthia, Germany, Spain, and they are intended to admit of the gradual separation of the lead from the roasted ore without melting down the charge, but merely heating it to such a degree that the reactions between lead sulphide and the sulphate or oxide may take place. The temperature requisite to produce this result is above the melting point of lead, and consequently the metal flows away from the heated mass along the sloping hearth to the point where it escapes into a receptacle placed outside the furnace.

The Flintshire furnace is represented by fig. 262 in vertical section, and in horizontal section by fig. 263.

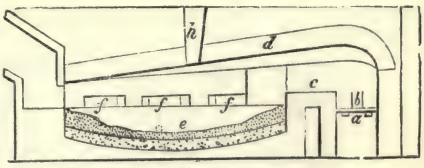


Fig. 262.

On each side of the smelting chamber of the furnace there are three doors (*fff*) by which the workmen have access to the charge for the purpose of stirring. The fireplace (*a*) is separated from the smelting chamber by the fire bridge (*c*). The hopper (*h*) in the arched roof (*d*) of the furnace serves for introducing the charge of ore. The hearth is nearly square, and it slopes down from the fire bridge and from the opposite end of the smelting chamber towards the centre, where it is about two feet deeper than the sill of the middle furnace door (*f*); the tap hole (*e*, fig. 262), is at a level with the bottom of the hearth, and through it both the reduced lead and the slag are run off into the cast-iron pan (*i*). The hearth of the furnace is formed of slag obtained in previous operations; this is heated until it assumes a pasty condition, and then spread into the required shape by means of paddles. The flues (*g g*) carry off the gaseous products from the fuel as well as those evolved by the treatment of the charge, and since there is a considerable quantity of lead carried off in the state of vapour, or as an extremely fine dust, the flues of the smelting furnaces are often connected with condensing chambers which serve no less for the recovery of lead that would otherwise be wasted, than for preventing injury to vegetation and animal life by its discharge into the air. In such instances several furnaces are connected together as shown in fig. 264, and the waste gas from all the furnaces (*a a a*) is led into a common flue (*c c c*) communicating with the condensing chamber (*e*) and the chimney (*h*).

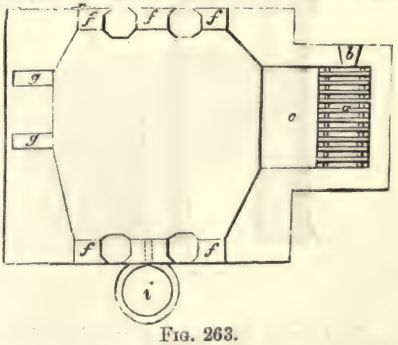


Fig. 263.

The ordinary charge of ore in these furnaces is about 20 cwt.: after being shot in through the hopper (*h*), it is spread uniformly over the upper part of the hearth and moderately heated during the space of two hours, while the furnace doors are closed and the draught checked by lowering the dampers of the flues. During this stage of the operation, termed the first fire, the ore is oxidised, and when this process has been carried far enough, the dampers are partly raised, fresh fuel added, and the heat increased to bright redness for running down the charge by the second fire, which is kept up for 25 minutes, during which time a considerable quantity of reduced lead is melted, and collects at the bottom of the hearth.

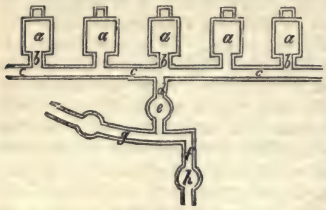
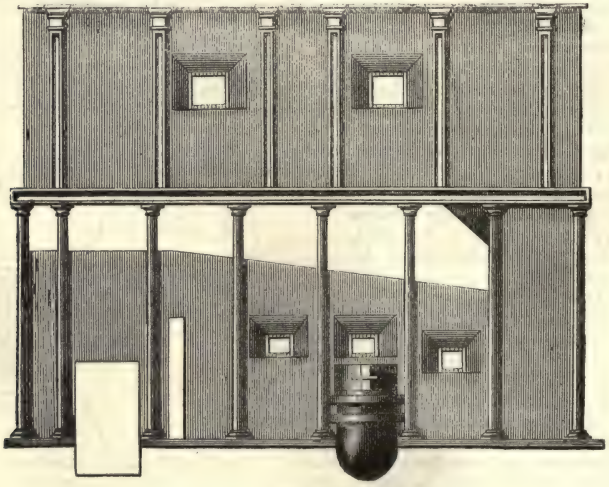


FIG. 264.

The furnace doors are then opened and the workmen throw some lime over the surface of the slag, which renders it sufficiently pasty to allow of being pushed back from the melted metal to the higher parts of the hearth. Meanwhile the furnace cools down a little, and the slag and ore upon the upper parts of the hearth are stirred with rakes, and after about three hours fresh fuel is added for the third fire, the dampers fully opened and the furnace doors kept closed for nearly an hour. This alternate heating and cooling of the furnace, and the manipulation of the slag and ore have the effect of facilitating the separation of the lead, and the addition of lime protects the melted metal from oxidation, besides rendering the slags less liquid, or as it is termed dry. After giving a fourth fire the doors are opened and the tap hole (*e*, fig. 262) is pierced so as to let the melted lead flow from the hearth into the pot (*i*). Some more lime is then added, and then the dried slag is pushed back and raked out of the doors at the back of the furnace.

The whole operation termed a smelting shift occupies about four hours and a half from the time of charging the furnace. In the north of England smaller charges are worked, varying from 12 to 14 cwt., and in Cornwall the charge is as much as 30 cwt. or even 3 tons.

Sometimes the operations of roasting and smelting are conducted in separate furnaces which are connected together, as shown by fig. 265, which represents the front or tapping side of the furnace.


FIG. 265.

This plan is followed in Cornwall, and the two operations of roasting and smelting are termed the calcination and the flowing. The calcining furnace has holes in the bed through which the roasted ore is raked down into an arched vault beneath. The flowing furnace is similar to that used in Wales, and the operation is conducted essentially in the same manner as the second stage of the treatment just described.

After tapping off the reduced lead which has melted and run down into the lowest part of the hearth, the melted slag is mixed with lime and coal dust, and when thus

rendered pasty or dried up as it is termed, it is spread upon the higher part of the hearth. Some scrap iron is generally added, which helps the reduction of lead sulphide, and fluor spar is added as a flux. The furnace doors are then closed and the charge melted down again. The lead oxide in the slag is decomposed partly by the carbon added in the shape of coal dust, and by the action of the iron upon lead sulphide, a further quantity of lead is produced, together with ferrous sulphide, that forms a regulus and retains greater part of the copper. In tapping the furnace, this regulus is separated and subjected to further treatment for separating any lead it may contain.

The reverberatory furnace employed at Bleiberg in Carinthia for lead smelting is represented by figs. 266 to 269. The hearth (*b*) is long and narrow, with a considerable inclination from one end to the other, and hollowed out so as to form a gutter-like channel as shown in the transverse section, fig. 269. The fireplace (*a*) is at the side of the hearth, and separated from it by a fire bridge, and the fire gas after passing through the working chamber of the furnace, escapes through the flue (*e*) into the chimney.

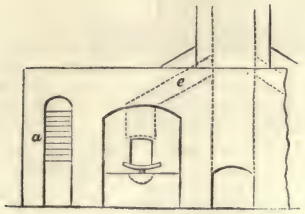


Fig. 266.

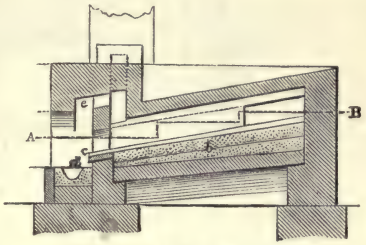


Fig. 267.

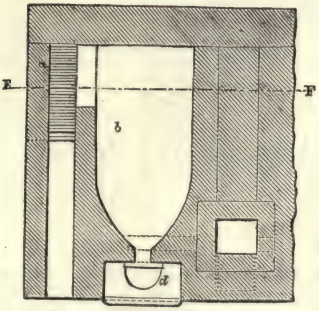


Fig. 268.

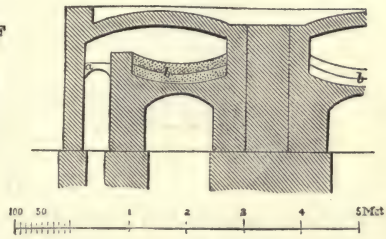


Fig. 269.

The hearth is formed of two layers, as shown in figs. 267 and 269, the lower one consisting of clay and the upper one of slag, rammed down and hardened by heat. These furnaces are generally built in pairs with a common chimney, as shown in fig. 266, which represents a front elevation. The sloping hearth is intended to afford an opportunity for the lead resulting from the reaction between lead sulphide and lead oxide or sulphate to flow out at once into the receptacle (*d*) placed outside the working door of the furnace. The quantity of ore worked does not amount to more than 3 or 4 hundredweight at each charge.

In working this furnace, the roasting operation is carried out very gradually, and when sufficiently far advanced, the heat is raised to bring about the reaction between the oxidised portion and the lead sulphide. The separation of the metal is promoted by vigorously stirring the mass, and increasing the temperature until the whole of the lead sulphide is decomposed and no more lead flows out into the receptacle (*d*). The lead which separates at first when the temperature is lowest is the most pure, and that obtained after raising the heat is less pure. When the pasty mass from which lead has ceased to run out begins to melt, it is mixed with coal dust and again heated strongly; the lead oxide it contains is thus reduced, and a further separation of lead takes place, until at last when the furnace has attained a full red heat, the slag remaining contains but very little lead.

This method of smelting is expensive on account of the time and labour it requires.

With pure ore rich in lead it yields lead of very good quality, but it would not be applicable in the case of ore containing admixtures of other minerals.

The reverberatory furnace employed for lead smelting in France is represented by figs. 270 to 272, the first being a longitudinal section on the line A B, fig. 271, the second a horizontal section on the line C D, fig. 270, and the third a transverse section on the line E F, fig. 270. The working doors, three in number, are placed on one side of the furnace, and the pot (*i*) for receiving the lead is opposite the middle door.

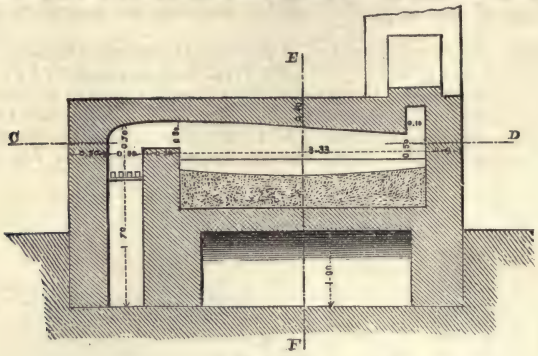


FIG. 270.

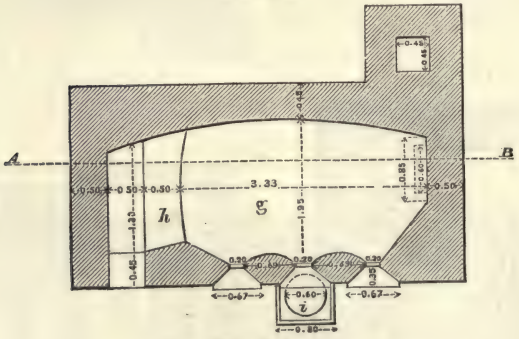


FIG. 271.

The fireplace is separated from the smelting chamber by the bridge (*h*), and the hearth (*g*), besides being slightly hollowed from end to end, as shown in fig. 270, slopes from one side of the furnace to the other, as shown in fig. 272, the lowest side being next to the receptacle (*i*).

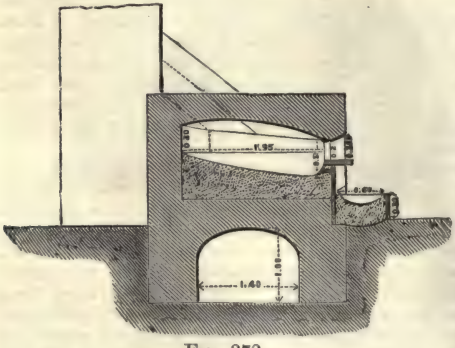


FIG. 272.

In working this furnace a charge of about one ton of ore is heated very gradually until a thick crust of lead sulphate has formed on the surface. The temperature is then reduced, and the charge stirred until at the end of about four hours it begins to soften, and globules of lead appear as the result of the reaction between lead sulphate and lead sulphide. At this stage a quantity of wood or small coal is thrown upon the mass, and it is actively stirred, while metallic lead runs into the well of the hearth, from whence it is tapped off into the pot (*i*). A second roasting then follows, and some coal or wood is thrown upon the charge in order to reduce the lead oxide, followed by further stirring to separate the reduced lead.

The chief point in which the French method differs from that practised in Carinthia consists in roasting the ore so that a much larger proportion of the lead sulphide is converted into sulphate, before the temperature is raised to the point at which the reaction between lead sulphate and lead sulphide takes place. Consequently there is only a small quantity of lead produced in this way, and the product of the reaction is chiefly lead oxide, as shown in the following equation:

$$PbS + 3PbSO_4 = 4PbO + 4SO_2.$$

The lead oxide thus formed is readily decomposed by carbon, the products being metallic lead and carbonic oxide, according to the following equation:

$$4PbO + 4C = 4Pb + 4CO.$$

Any lead sulphate that remains in the charge is partly converted by the carbon of the wood into sulphide, with formation of carbonic dioxide, and then by reaction with another portion of the sulphate, yields lead oxide and sulphurous oxide:

$$3PbSO_4 + PbS = 4PbO + 4SO_2.$$

A rude form of reverberatory furnace has long been used in Spain under the name of boliche for the smelting of lead ore. It consists of two arched chambers, only one of which is used for the treatment of the ore, and the other probably serves the purpose of regulating the draught. The hearth of the boliche is sloping, and at one extremity there is a well connected with a receptacle outside the furnace, into which the reduced lead runs out by tapping.

The slag produced in smelting lead ores in reverberatory furnaces is always rich in lead; but as will be seen from the following table of analyses, it varies in composition according to the nature of the gangue substance in the ore.

	Flintshire	Derbyshire			Poullaouen	
	Tookey				Berthier	
Silica	13·52	—	—	—	—	24·
Alumina	3·01	—	—	—	—	—
Ferric oxide	2·86	15·4	5·6	4·5	2·0	14·
Zinc oxide	7·52	7·2	8·0		2·0	27·
Lime	12·68	16·0	14·7	8·0	8·0	—
Lead oxide	48·87	—	—	—	—	26·5
Lead sulphate	9·85	12·0	30·0	22·0	9·0	3·0
Barium sulphate	—	22·0	24·4	25·	30·0	—
Calcium sulphate	—	1·6	5·6	22·5	33·0	—
Calcium fluoride	—	7·2	8·5	16·	13·6	—
Lead sulphide	0·90	17·0	2·	—	—	5·0
	99·66	98·4	98·7	98·0	97·6	—

As already mentioned, the ores of lead always contain other earthy and metallic compounds which interfere with the reactions by which lead is reduced, and thus in various ways the result obtained in smelting such impure ores is different from that obtained when pure galena is operated upon in the reverberatory furnace.

Ores containing only small amounts of calcium carbonate can be worked without inconvenience, and even when there is from 10 to 12 per cent. of this substance, it facilitates the decomposition of the lead sulphide, besides preventing the charge from becoming too liquid.

Barium sulphate is quite inert during the smelting operation, and it is objectionable only as mechanically hindering the reaction of the lead sulphate or oxide with the unoxidised sulphide. When the ore contains 15 per cent. of this substance, it is not suitable for smelting in a reverberatory furnace.

Fluor spar acts much in the same way as calcium carbonate, but it is beneficial when associated with barium sulphate, since it acts as a flux upon that substance.

Quartz and silicates are very injurious even when amounting to only 5 or 6 per cent. of the ore, and when they amount to 12 per cent. no metal can be obtained by heating lead ore in the reverberatory furnace. During the operation of roasting these substances do not react upon the lead compounds, but when the temperature is raised in the smelting operation, silica combines with lead oxide before this reacts with lead sulphide, forming lead silicate, which melts and renders the whole charge so liquid that it cannot be worked.

Zinc sulphide in the form of blende is often associated with lead ore, and when the amount does not exceed 10 or 15 per cent., its presence does not much interfere with the working of the reverberatory furnace; it is objectionable chiefly by its conversion into oxide and sulphate, which prevent the intimate mixture of the lead compounds. The blende which escapes oxidation during the first stage of the operation reacts afterwards upon the lead oxide, producing metallic lead, zinc oxide and sulphurous oxide. When carbonaceous materials are added in the smelting, the zinc oxide is reduced together with lead oxide, and, the zinc being volatilised, a considerable quantity of lead is carried away by the zinc vapour.

The presence of a small amount of iron pyrites does not seriously interfere with the smelting in reverberatory furnaces. In roasting, the pyrites is oxidised more rapidly than galena; the portion that escapes oxidation is afterwards useful in reducing lead oxide, but in the subsequent stage the ferric oxide disseminated through the mass interferes with the melting of the lead compounds. A large amount of pyrites is very prejudicial, since the unoxidised portion would form a very fusible compound with the lead sulphide and prevent its decomposition. Arsenical pyrites is still more objectionable, because the lead obtained is contaminated with arsenic and the presence of this substance in lead augments the loss both of lead and silver in cupellation.

Antimonous sulphide is always very injurious even when there is only 2 or 3 per cent. It undergoes the same changes as lead sulphide, a portion of the antimony is reduced and alloyed with the lead, rendering the metal hard besides causing loss of lead and of silver in cupellation. Moreover the compounds of antimony form very fusible compounds with lead, which cannot be reduced, and owing to the great volatility of antimony as well as of its oxide and sulphide, the loss of lead and silver is very much augmented.

The presence of copper pyrites renders lead ores unfit for treatment in reverberatory furnaces; even when the amount is so small that the reactions proper to this method are not interfered with, the lead obtained retains some copper, and is on that account less valuable.

Ferrous carbonate acts only as a mechanical obstacle to the working in the furnace, as it is gradually converted into ferric oxide: in the latter stage of the operation this interferes with the melting of the slag and retards the reactions until almost all of the lead sulphide is oxidised; in small amount ferrous carbonate is rather advantageous than otherwise.

Besides the ores containing lead in the state of sulphide some others occur in various localities which contain either lead carbonate or lead sulphate. Generally they occur together with ores containing galena and are worked with them, but in a few instances these oxidised ores are sufficiently abundant to be smelted separately. At the Russian lead works in the Altai mountains large quantities of ore are smelted which contain from 8 to 20 per cent. of lead in the state of carbonate associated with cupreous minerals, quartz, heavy spar, and slate. Shaft furnaces are used and the ore is smelted with limestone, common salt, and slag from previous operations.

Ores containing lead carbonate are also worked to some considerable extent in Spain, either in the Castilian blast furnace (p. 365) or the furnace in which a draft is produced by means of a chimney (p. 366).

Lead sulphate occurs even less frequently than lead carbonate in such quantity as to be worked separately; but a large quantity of lead sulphate is produced in calico works. Several methods have been proposed for treating this substance. That of Rivot and Phillips consists in roasting the lead sulphate until sulphuric acid is no longer given off, then adding about 20 per cent. of quartz and some coal dust, and heating the mass until it melts and ceases to give off sulphurous and sulphuric oxides. In this way the lead is for the most part converted into silicate, which can be smelted with the addition of scrap iron or with lime and coke in a shaft furnace. In both cases the yield of lead falls short of the quantity that should be obtained and the cost of the operation is considerable. By smelting the silicate with iron pyrites less lead is retained by the slag, but a regulus is produced unless the pyrites is very intimately mixed with the silicate. The iron pyrites is then decomposed in the smelting, sulphur being driven off, and the ferrous sulphide reacts with the lead silicate, producing lead sulphurous oxide and ferrous silicate.

Most lead ores contain some silver, and since this metal is always reduced in smelting argentiferous lead ores, the lead thus obtained is often of great value as a source of silver. The methods of cupellation and crystallisation by which the two metals are separated will be described in detail under the head of 'Silver.'

In the separation of these metals by one method the lead is entirely converted into lead oxide or litharge, and in order to obtain metallic lead this oxide has to be reduced by an operation analogous to the smelting of oxidised lead ores either in reverberatory furnaces or shaft furnaces. On the continent litharge is frequently

smelted in shaft furnaces, since the reduction is rapidly effected and less labour is required, but the lead thus obtained still contains some copper and antimony and is inferior in quality to that reduced in reverberatory furnaces.

The shaft furnaces employed for the reduction of litharge are similar to those in which lead ore is smelted, but generally they are not so high and they are worked with flame issuing from the throat. To prevent loss of lead, lumps of coke are piled up above the throat of the furnace, so as to be heated by the flame sufficiently to reduce the lead oxide carried up by the ascending gas.

The reduction of lead oxide is in this country generally effected in a reverberatory furnace of the kind represented by figs. 273 and 274. A is the fireplace, B the ash pit, C the fire bridge, D the hearth, E the working door, F the iron gutter by which the lead is run off into the pot G.

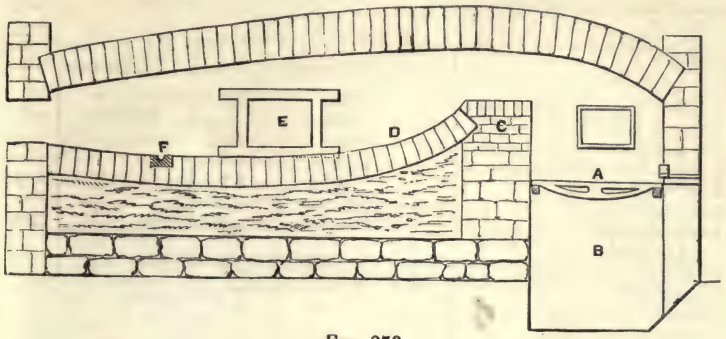


FIG. 273.

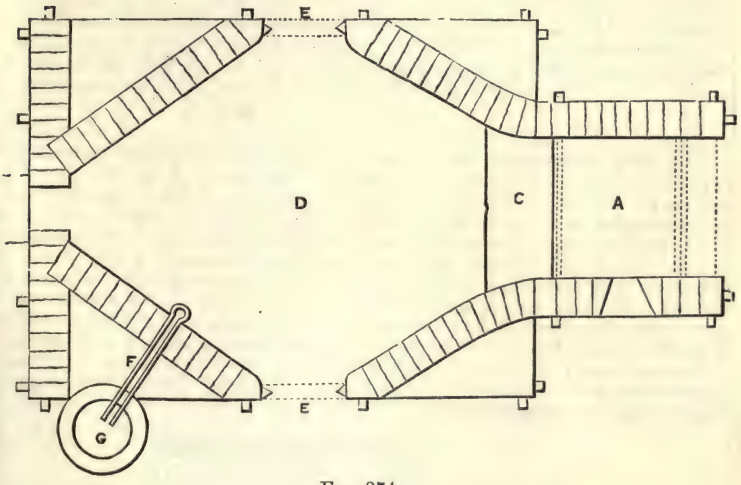


FIG. 274.

The oxide is mixed with about 10 per cent. of coal dust and placed on the hearth near the fire bridge where it is soon reduced, and the metal flows down to the lower part of the hearth. To prevent the action of the lead oxide upon the material of which the sole is made, a layer of small coal is spread upon it before the charge is put in.

Condensation of lead fume.—Owing to the volatilisation of lead sulphide and metallic lead which always takes place in smelting lead ores either in shaft furnaces or reverberatory furnaces, the gas escaping from the smelting furnaces carries away a large quantity of lead, for the collection of which very efficient means of condensation are required. In some cases the condensation is effected by making the gas pass through flues of great length, where the vaporised lead is gradually deposited together with that held in suspension in the state of finely divided particles. The quantity of

lead volatilised in smelting lead ores is very much influenced by the presence of other volatilisable substances in the ore, such as zinc, antimony, and arsenic, and these substances are found chiefly in an oxidised condition together with the lead in the deposit formed in the flues, which is commonly known by the name of lead fume. This frequently contains lead in the metallic state, also lead oxide as well as sulphate, carbonate, and sulphide. Some of these compounds are probably formed by the action of atmospheric air upon the vaporised lead, or by the action of sulphurous oxide and sulphuretted hydrogen within the flues. Since the lead in this deposit amounts to from 1 to 10 per cent. of the total amount in the ore smelted it is evident that the fume is worth collecting independently of the deleterious effect that would result from its being allowed to escape into the atmosphere. The following table gives the composition of the fume from several lead works, where the ores are smelted in shaft furnaces and reverberatory furnaces.

	Pontgibaud			Alston moor	Redruth	Freiberg
	Rivot			Berthier		
Lead	—	—	55·4	—	—	—
Lead oxide	—	66·5	3·7	10·20	71·21	27·9
Lead carbonate	35·0	—	—	—	—	—
Lead sulphate	39·0	—	13·0	65·60	—	13·0
Lead sulphide	4·5	—	—	1·40	—	—
Zinc oxide	2·7	12·0	3·1	13·80	—	49·5
Zinc sulphate	2·3	—	—	—	—	—
Arsenous acid	1·5	1·1	1·5	—	—	2·1
Cupric oxide	—	—	—	—	0·2	—
Ferric oxide	—	3·0	13·0	3·40	trace	—
Sulphur	—	—	8·9	—	—	—
Sulphuric acid	—	17·0	—	—	—	—
Carbonic dioxide	—	—	—	—	—	7·0
Substance insoluble in acids	13·2	—	—	5·60	21·8	—
	98·2	99·6	98·2	—	—	—

One of the arrangements for condensing lead fume by mechanical means, known as Stokoe's condenser, is represented by fig. 275. At the top of the flue (A) which receives the gas discharged from the smelting furnaces is a fan, capable of being driven at a high speed, by means of which the gas is drawn out of the flue and forced into a chamber (F F, F F) containing water at the bottom, and separated by partitions into six or more compartments; so that the gas is made to travel up and down in the direction of the arrows and come several times in contact with the water in the chamber. In its passage through the chamber to the outlet (H) the gas has also to pass several times through the horizontal perforated shelves (A A), covered with layers of pebbles or other fitting material, and at the same time it is exposed to the action of a shower of water falling from the cistern (M) at the top of the chamber. In Stagg's condenser the gas is drawn out of the furnaces by a powerful double-acting air-pump, which also forces it through water.

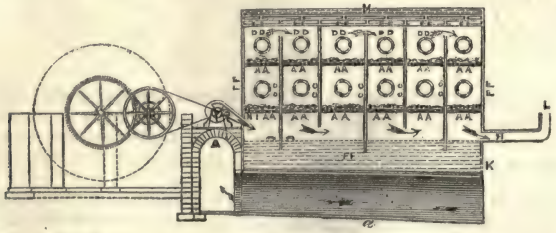


FIG. 275.

Before the lead obtained from certain kinds of poor ores, or by smelting in blast furnaces, can be operated upon for the extraction of the silver it contains (p. 384), a preliminary purification is requisite for the purpose of separating any antimony, tin, or

copper it may contain, together with other impurities, which render the metal hard and unfit for the process of desilverising. The following table shows the composition of different kinds of hard lead, and the nature of the impurities it contains:—

	English	Spanish	Hartz		Pontgibaud	Freiberg
	Richardson	—	Streng and Overbeck		—	Karsten
Lead . .	99·27	95·81	83·65	77·75	91·4	91·51
Antimony . .	0·57	3·36	16·00	21·27	8·2	5·32
Arsenic . .	—	—	—	—	0·4	1·02
Copper . .	0·12	0·32	0·13	0.16	—	0·90
Iron . . }	0·04	0·21	0·30	0·49	—	0·62
Zinc . . }		—				
Sulphur . .	—	—	—	—	—	0·20

Some kinds of lead are so hard that they are unfit for many of the ordinary purposes to which this metal is applied, and for this reason also the softening operation is essentially necessary. It consists in exposing the melted metal to the oxidising action of the air for a length of time which depends upon the nature and amount of the impurities to be removed.

The furnace employed for this operation of calcining or improving is represented by figs. 276 to 278. It is a reverberatory furnace, the hearth (D) of which

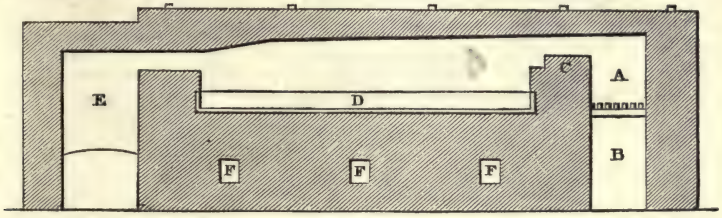


Fig. 276.

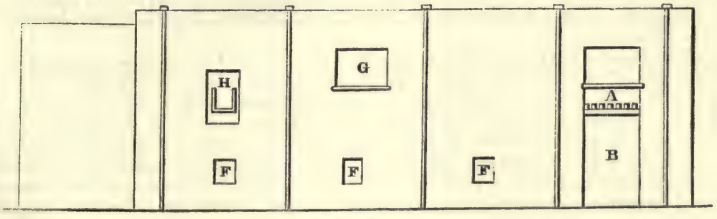


Fig. 277.

consists of a cast-iron pan, separated by the bridge (C) from the fireplace (A). Below the bed are several channels (F F F) for the escape of moisture, and at the side there is a working door (G), as well as an opening (H), by which the softened lead can be run off when the operation is at an end.

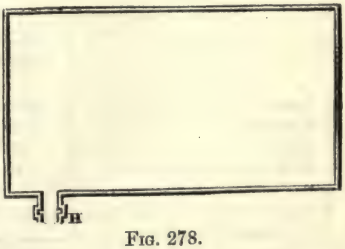


Fig. 278.

The charge varies from nine to ten tons, and as soon as the furnace is at a working heat, the surface of the melted metal becomes covered with a scum or dross, consisting of metallic oxides, which is skimmed off and removed through the working door (G). When the lead is very impure, this scum often floats in a semi-liquid state on the surface of the lead, and then it requires the addition of some lime, which renders it dry and capable of being removed.

As the operation progresses, a small quantity of the lead is dipped out with a ladle, run into a mould, and examined when cold, to ascertain whether it is sufficiently

purified. If it presents at the surface a flaky, crystalline appearance, and is soft, the charge is ready to be run off. The spout (H) of the iron pan is then opened, and the metal run into moulds.

An improved form of furnace for softening lead by calcination is represented by figs. 279 and 280. The hard lead is melted in the pot (*a*), heated by a fire at *b*, and

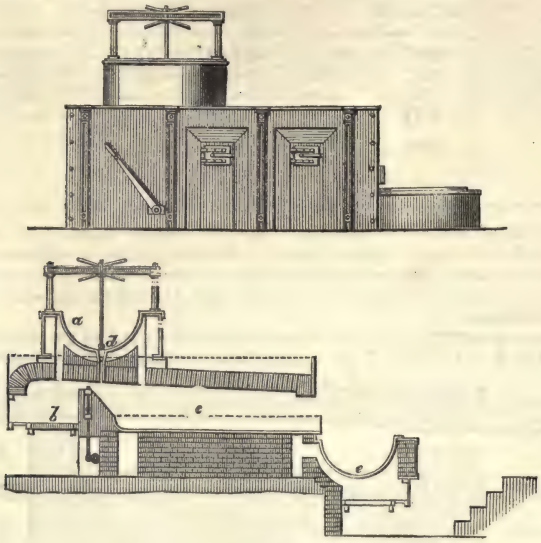


FIG. 280.

the calcining pan (*c*) is fed with melted lead by raising the plug (*d*). When the softening is completed, the metal is run into the pot (*e*), and then cast in moulds.

The amount of soft lead thus obtained from different kinds of hard lead varies from 76 to 93 per cent.

The use of a mixture of sodium nitrate, soda ash, and lime, has been proposed with the object of shortening the time requisite for softening lead by oxidation; but it is doubtful whether any real advantage is gained in this way, especially if it be the case that the antimony in lead collects as an alloy at the surface in consequence of its lower specific gravity, and is therefore readily acted upon by atmospheric oxygen.

The dross obtained in the softening contains a considerable amount of antimony, together with some copper, iron, and a certain proportion of lead, yielding when reduced by heating it with carbonaceous material, an alloy that has the following composition:—

	Without alkaline flux	Reduced with addition of soda ash	Alloy from dross of first calcination		Alloy from dross of second calcination	
			English	Spanish	English	Spanish
Lead . .	82·88	58·70	86·53	64·98	52·84	56·60
Antimony .	16·09	40·66	11·29	29·84	47·16	43·40
Copper . .	·68	·32	traces	5·90	trace	traces
Iron . .	·35	·32	0·34	0·20	trace	traces
	100·00	100·00	98·16	100·92	100·00	100·00

The addition of a little soda ash as a flux facilitates the reduction, but the metal obtained is too hard to be used for many purposes. By calcination, the impurities may be separated from the lead, and the dross from this operation gives, on reduction, an alloy containing a still greater proportion of antimony, which can only be used for making type metal or as bullets.

Richardson proposed to act upon the dross of the second calcination with acetic acid, so as to dissolve the lead and obtain sugar of lead. The residue was then reduced in the same way as antimony ores. The same process serves for the separation of tin. In some cases, the dross may be turned to account for preparing lead antimonate, which is used as a pigment under the name of Naples Yellow.

Uses.—Lead is one of the most useful metals, and it is applied to a great many purposes, such as the lining of cisterns, roofing, etc.; in the form of pipe it is used for the supply of water to houses and factories; very thin sheets of lead are used for packing articles requiring to be kept dry, and in chemical works lead is employed for a number of purposes, such for instance as the construction of sulphuric acid chambers. Many of the alloys of lead with other metals have an equally wide range of utility.

Compounds.—Lead is divalent in most of its compounds. There are three definite oxides; a suboxide Pb_2O which is of little importance, the protoxide PbO is a powerful base, forming saline compounds with acid oxides, some of which are isomorphous with the corresponding salts of barium and strontium, and the dioxide PbO_2 which has to some extent the character of an acid oxide. There is but one sulphide PbS, corresponding to the protoxide. With chlorine, bromine, iodine, and fluorine, lead forms compounds represented by the formulæ $PbCl_2$, $PbBr_2$, PbI_2, PF_2. Many lead salts are insoluble in water, as, for instance, the sulphate, phosphate, arsenate and carbonate; those which are soluble have a slight acid reaction even when neutral, and a peculiar sweet taste; all lead salts are poisonous.

Melted lead mixes readily in all proportions with other metals the melting points of which are lower than that of lead or not much above it, and with some of them it forms definite alloys, the melting points of which differ from those of the constituent metals. Lead also unites with metals of much higher melting point, but in many instances the lead can be separated from such mixtures by heating them to the temperature at which leads melts. This process is termed liquation, and is taken advantage of in metallurgy. Several of the alloys of lead are of great importance for various practical applications; thus the alloy of lead with about one third its weight of antimony constitutes type metal. Pewter is an alloy of lead with one fourth its weight of tin; the different kinds of solder are alloys of lead and tin in various proportions. Lead also enters into the composition of the alloys known as Britannia metal, Queen's metal, etc., and some kinds of bronze contain lead. The alloy of lead with about one-fiftieth of its weight of arsenic is used for making shot.

Lead and zinc may be mixed together in any proportions when melted, and the alloy is harder than lead, takes a high polish and is very malleable. At a high temperature the zinc is volatilised together with some of the lead. The presence of a small proportion of zinc in lead renders the metal less capable of being rolled into sheets.

The other alloys of lead will be described under the heads of the different metals.

LEAD OXIDE.

Formula PbO. Molecular Weight 223.

History.—This substance, commonly called litharge or massicot, was known at a very remote period under the names of λιθάργυρος and σκωρία μολύβδου, *plumbum ustum*, etc.

Occurrence.—Lead oxide occurs naturally as lead ochre in volcanic districts and associated with lead ores, but not to any great extent. It is obtained by oxidation of lead as a by-product of the cupellation method of extracting silver from argentiferous lead.

Characters.—Lead oxide when pure is a lemon-yellow substance, but is met with in several different forms which depend upon the conditions under which it is produced. When in the crystallised state, in which it is obtained by the solidification of the melted substance, it has a pale reddish-yellow or buff colour, the particular shade varying according to the state of aggregation. In this state it is called litharge. When formed by the oxidation of lead at a temperature below the melting point of the oxide, it forms a dull yellow amorphous powder known as massicot. The specific gravity varies from 9·2 to 9·5. Lead oxide melts at a red heat, forming a dark red transparent liquid. It is stated by Fournet to be volatilised at a white heat, but less readily than metallic lead.

Lead oxide is decomposed when heated to redness with carbon or carbonaceous substances, and in some cases at lower temperatures, metallic lead being produced

together with carbonic dioxide; it is also decomposed when heated with iron, zinc, copper, etc., to a sufficiently high temperature, and is on this account frequently useful as an oxidising agent in some metallurgical operations. Melted lead oxide also dissolves a number of other oxides which cannot be melted themselves or only at very high temperatures. With silica or silicates it readily combines, forming a very fusible glass which is colourless unless it contains a very large amount of lead. Lead silicate is a constituent of several kinds of glass, and especially that known as flint glass or crystal.

Lead oxide combines readily with most oxyacids forming salts, many of which are soluble in water; the oxide also dissolves in solutions of caustic potash, soda, baryta, or lime; it is also soluble to some extent in water, but requires from 7,000 to 12,000 parts of water for solution.

Lead hydrate PbH_2O_2 is a white pulverulent substance which loses water when heated above 100°, and is converted into anhydrous oxide. When metallic lead is immersed in pure water lead hydrate is formed, and to some extent dissolved. The hydrate readily absorbs carbonic dioxide, and is converted into carbonate; it also absorbs ammonia and retains it in combination.

Preparation.—Lead oxide is prepared on the large scale by the oxidation of melted lead, and it is obtained as a product of the operation by which silver is separated from lead. (See Silver.)

Uses.—In the forms of litharge and massicot, lead oxide is used for preparing drying oil, by boiling linseed oil with a small quantity of the oxide. It is also used in the preparation of a cement for repairing the stone work of buildings by mixing with 8 or 10 times its weight of brick dust, and sufficient linseed oil to form a stiff paste. This preparation is called Dhil mastic; it rapidly hardens by exposure to the air. Lead oxide is also used as a flux in assaying, and for several pharmaceutical preparations.

LEAD PEROXIDE.

Formula PbO_2. Molecular Weight 239.

This substance occurs naturally as plattnerite in brilliant prismatic crystals, and is formed when chlorine is brought into contact with lead oxide suspended in water, or when the oxide is acted upon by melted potassium chlorate. A more ready way of obtaining the peroxide is to digest red lead with weak nitric acid. As prepared artificially it is a brown powder insoluble in water and dilute acids; it is decomposed by strong hydrochloric acid and converted into lead chloride with evolution of chlorine $PbO_2 + 4HCl = PbCl_2 + 2H_2O + 2Cl$. It reacts violently with sulphurous oxide, absorbing the gas and forming lead sulphate $PbO_2 + SO_2 + PbSO_4$, with nitrous acid it forms lead nitrate. A mixture of the oxide with one-sixth its weight of sulphur takes fire when rubbed. Lead peroxide when heated gives off half its oxygen, and it acts as an oxidising agent towards many organic substances.

Lead peroxide combines with bases, forming a series of compounds called plumbates, in which it acts the part of an acid. It has also to a slight extent the power of forming salts with acids.

Red Lead.—This substance is a compound of lead oxide with the peroxide, generally in proportions approximating to the formula $PbO_2 2PbO$. It occurs naturally as minium together with ores of lead, and is formed when lead oxide is exposed for some length of time to the action of atmospheric air at a dull red heat insufficient to melt the oxide.

Characters.—Red lead is a scarlet crystalline powder. The specific gravity varies from 8·62 to 9·08. When heated the colour becomes temporarily darker, and gradually passes into violet, becoming red again on cooling: at a red heat, oxygen is given off and lead oxide remains. Red lead is also reduced by many oxidisable substances such as sulphurous oxide, sugar, and other organic substances; when mixed with hydrochloric acid it is converted either into lead chloride, peroxide and water,

$$PbO_2 + 2PbO + 4HCl = 2PbCl_2 + 2H_2O + PbO_2,$$

or into lead chloride, water and chlorine according to the proportion of acid,

$$PbO_2 + 2PbO + 8HCl = 3PbCl_2 + 4H_2O + 2Cl.$$

When red lead is digested with glacial acetic acid, or cold concentrated solutions of phosphoric acid, or arsenic acid, it dissolves, forming solutions containing salts of

the peroxide which are readily decomposed. Strong acids decompose red lead; sulphuric acid converting it into sulphate with evolution of oxygen; nitric acid dissolves the lead oxide and leaves the peroxide as a brown powder.

Preparation.—Red lead is prepared on a large scale by oxidising lead in a reverberatory furnace, at a temperature insufficient to melt the lead oxide formed. By this means the lead oxide is obtained in the state of massicot, which is then ground to a fine powder, again placed in a reverberatory furnace, and exposed for two days to a carefully regulated temperature until it has absorbed sufficient oxygen and a portion taken out has a bright red colour when cold. The furnace is then closed and allowed to cool slowly.

LEAD SULPHIDE.

Formula PbS. Molecular Weight 239.

This substance occurs very abundantly as galena, and the most important ores of lead consist chiefly of this mineral.

The following table gives the composition of galena from different localities:

		England	Hanover	Bohemia		Schemnitz
		Thomson	Westrumb	Lerch		Beudant
Lead	86·61	85·13	83·00	81·80	83·61	79·60
Silver	—	—	·08	—	—	7·00
Iron	—	0·50	—	—	—	—
Zinc	—	—	—	3·59	2·18	—
Sulphur	13·39	13·02	16·41	14·41	14·18	13·40
	100·00	98·65	99·49	99·80	99·97	100·00

The amount of silver in galena generally ranges between 0·01 and 0·03 per cent., but sometimes is as much as 0·5 or even 1 per cent. Argentiferous galena almost always contains a recognisable amount of gold.

Lead sulphide has in the crystalline state a dark grey colour and high metallic lustre; the specific gravity is from 7·25 to 7·7. The sulphide formed by melting together lead and sulphur, and by melting the precipitate obtained by treating solutions of lead salts with sulphuretted hydrogen, has a specific gravity of 7·505.

Lead sulphide melts at a full red heat, above the melting point of lead; it volatilises at a higher temperature, and if kept out of contact with air sublimes without decomposition. Hence it is often found in this state in smelting furnaces in which ores containing lead have been smelted.

When moderately ignited in contact with atmospheric air lead sulphide is gradually oxidised, and gives off part of its sulphur as sulphurous oxide, with production of lead oxide and some lead sulphate.

The following analyses of roasted galena show the nature of the material operated upon in different localities:

	Pezey	Holzapfel		Pontgibaud		
Lead oxide	18	35	31·0	52·6	16·9	62·9
„ sulphate	86	19	8·0	8·0	12·1	—
„ sulphide	10	4	11·8	—	—	—
Ferric oxide	—	6	9·0	13·0	21·3	4·9
Zinc oxide	—	27	30·2	9·0	21·6	3·7
Manganous oxide	—	2	—	—	—	—
Arsenic oxide	—	—	—	0·4	1·0	—
Barium sulphate	—	—	—	14·0	19·8	0·7
Silica	—	7	10·0	3·0	6·2	23·9
Lime	—	—	—	—	—	3·1
	114	100	100·0	100·0	98·9	99·2

Lead sulphide is insoluble in most dilute acids; when boiled with dilute nitric acid, it is converted into nitrate with separation of sulphur. Strong hydrochloric acid converts it, with the aid of heat, into chloride, with evolution of sulphuretted hydrogen; fuming nitric acid converts it into lead sulphate. When lead sulphide is heated with lead oxide in the proportion of 2 molecules to 1 of sulphide, the whole of the lead is reduced and sulphurous oxide given off:

$$PbS + 2PbO = 3Pb + SO_2;$$

melted with alkaline carbonates, part of the lead is reduced to the metallic state.

Lead sulphide is decomposed when heated to a full red heat with metallic iron, according to the equation:

PbS	+	Fe	=	FeS	+	Pb.
239		56		88		207

The temperature must be sufficient to melt the ferrous sulphide; and unless excess of iron is present, part of the lead sulphide combines with the ferrous sulphide formed, producing a regulus in which the proportion of lead to iron varies according to circumstances. In smelting ores containing galena, the decomposition of lead sulphide is sometimes effected by means of metallic iron; and in such cases there is generally obtained, together with metallic lead, a regulus containing lead which requires to be subjected to further treatment for extracting the lead. Lead sulphide is partially decomposed in a similar manner when melted together with ferrous silicate, and ferrous sulphide is formed which combines with the undecomposed lead sulphide, forming a regulus. Both these methods of decomposing lead sulphide are employed in the smelting of lead ores.

Lead sulphide combines readily with ferrous sulphide when the two substances are brought into contact at a high temperature in the melted state. The product thus obtained is of variable composition and is termed regulus. In smelting poor lead ores the production of such a mixture of sulphides is often practised with the object of separating the lead from the earthy constituents of the ore and obtaining it in a more concentrated condition. If the ore does not naturally contain sufficient ferrous sulphide, it is mixed with iron pyrites before smelting.

LEAD SULPHATE.

Formula $PbSO_4$. Molecular Weight 303.

This substance occurs naturally both in a crystallised state, as anglesite and in amorphous masses together with galena. Some lead ores contain a considerable amount of lead sulphate. It is also produced in considerable quantity as a secondary result of the preparation of aluminic acetate for calico printing works.

Lead sulphate is almost insoluble in water, but it dissolves slightly in nitric acid, and freely in solutions of ammoniacal salts, especially ammonium acetate. It is dissolved also by concentrated sulphuric acid to some extent. Hydrochloric acid dissolves it with decomposition, and the hot solution deposits crystals of lead chloride. It bears a high temperature without decomposition, but when heated together with carbon it is reduced, and, according to the proportion of carbon, the lead is separated either in the state of metal, as sulphide or as oxide.

LEAD CARBONATE.

Formula $PbCO_3$. Molecular Weight 257.

History.—The preparation of white lead, which consists chiefly of this substance, was described by Dioscorides in the fourth century before Christ, and at a later period by Theophrastus, Pliny, and Vitruvius. The Arabians prepared white lead. Geber writing in the eighth century recommended for its preparation exposing lead to the vapour of vinegar. The art was afterwards introduced into Venice, Holland, England, Germany, and France.

Occurrence.—Lead carbonate occurs naturally in a well-crystallised condition, but in comparatively small quantity, as cerusite, a mineral found in Scotland, Germany, France, etc.

Composition.—The native carbonate is a neutral anhydrous salt having the composition represented by the formula given above; but the precipitate formed on adding a solution of alkaline carbonate to solutions of lead salts is a compound of the carbonate with lead hydrate, and the composition varies according to the conditions of

temperature and concentration under which it is produced. The artificially prepared lead carbonate, commonly called white lead, is also a basic salt, which may be regarded as a combination of neutral lead carbonate with hydrated lead oxide in various proportions approximating to one or other of the following formulæ:

$$2PbCO_3.PbH_2O_2, \qquad 3PbCO_3.PbH_2O_2, \qquad 5PbCO_3.3PbH_2O_2.$$

Phillips found one sample to have a composition represented by the formula $5PbCO_3.PbH_2O_2$.

Characters.—In the crystallised state, as it sometimes occurs naturally, lead carbonate is a transparent, colourless, brittle substance. It frequently forms fibrous or compact opaque masses; it has a specific gravity varying from 5·5 to 6·4.

The artificially prepared hydrocarbonate is a brilliant white pulverulent substance insoluble in pure water, but soluble in water containing carbonic acid, as well as in solutions of caustic potash or soda; it is also easily soluble in nitric acid or acetic acid, the solution being attended by effervescence. It is poisonous; is decomposed by sulphuretted hydrogen and ammonium sulphide, black lead sulphide being formed, and on this account it cannot be employed as paint in the vicinity of places where the atmosphere is contaminated with sulphuretted hydrogen gas, zinc white or baryta white being invariably used in such cases, since neither of these latter is blackened by sulphuretted hydrogen. Heated to dull redness, white lead loses carbonic acid and water, and is converted into lead oxide, which absorbs oxygen when heated to redness in the air, yielding very pure red lead.

Preparation.—Several methods are in use for preparing white lead, known respectively as the Dutch, French, and English methods, in each of which lead carbonate is formed by the decomposition of a basic compound of lead oxide with acetic acid. In order to obtain white lead of good quality it is desirable that the lead employed should be free from copper.

Dutch Method.—Metallic lead is converted into basic lead carbonate by the joint action of acetic acid, carbonic acid and atmospheric oxygen. This method is the oldest, and is still the one most practised. Metallic lead is melted in a cast-iron cauldron (A), over which is a sheet-iron hood (A′), through which the lead vapour is carried into the chamber (A″). The hood can be closed by a couple of sliding doors (B), an arrangement that is very necessary in melting down old lead, which gives off a good deal of dust. As soon as the lead is melted, it is ladled out, and cast in moulds into thin plates 16 inches long, 4 inches wide, and from $\frac{1}{16}$ to $\frac{1}{8}$ in. thick. These plates thus obtain a rough surface which facilitates the ensuing process of oxidation of the metal under the influence of acetic acid vapour. When plates of this kind are used, they are rolled up into loose coils. In order to secure the exposure of a considerable surface, Besançon recommended the use of moulds with rectangular furrows, so that the lead castings have the form as shown on a larger scale in fig. 282, and in the manufacture of white lead this plan is now generally adopted. The advantage of using the lead in this form of grates is that more surface is exposed, and the circulation of the vapour through the stacks is facilitated. The casting of the grates is accelerated by placing the moulds upon a rotatory disc (C) fig. 281, which the caster turns round directly a mould has been filled, and a second workman empties the moulds that have been filled.

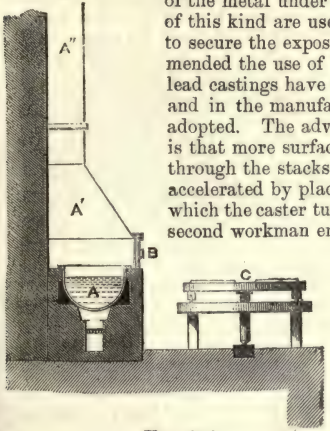


Fig. 281.



Fig. 282.

The next operation consists in exposing the lead castings to the simultaneous action of moist air, carbonic acid, and acetic acid vapour at a temperature of 35° to 60°.

The carbonic acid requisite for this purpose is often produced by the fermentation of horse dung mixed with straw, and large quantities of the lead castings are piled up with alternate layers of such materials in pits or brick chambers, where they are left for several weeks. The heat evolved by the fermenting material and by the oxidation of the lead is sufficient to keep up the temperature of the stack to the requisite degree.

The dung baths (fig. 283, *a a*) consist of rectangular chambers about 20 feet high and 13 feet square. Two rows of 6 or 8 chambers are built together back to back.

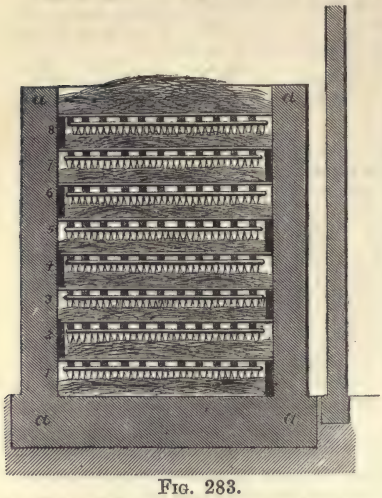


Fig. 283.

Charging the Chambers.—The bottom of each chamber is first covered with a layer of stable litter, upon which are placed a number of glazed earthen pots each containing about half-a-pint of vinegar. Five or six layers of lead gratings are laid above the pots, then several pieces of wood, and a layer of planks above. Upon this layer (No. 1, fig. 283) some more horse dung is spread with a similar layer of pots and lead gratings above it, and in this way a stack is built to the top of the chamber, a thick layer of horse dung being spread over the whole. In order to promote the circulation of air through the stacks, a space is left between one end of each layer and the wall of the chamber alternately at opposite sides, as shown in the vertical section, fig. 283.

In the place of horse dung, which must contain a sufficient quantity of straw, spent tan may be used, the action in both cases being due to the development of heat and carbonic acid by the decomposing organic substances. The heat causes evaporation of vinegar and water, which convert the lead in contact with atmospheric oxygen into basic lead acetate, and this salt is converted by the carbonic acid in the air into basic lead carbonate, or white lead, the neutral lead acetate formed at the same time being also converted by the moist and warm carbonic acid into carbonate, with liberation of acetic acid. The range of temperature best suited for this process is from 40° to 50°. In the centre of the stacks, especially at the beginning, when the fermentation is very active, the temperature rises as high as 90° or 100°, but near the sides of the chamber the temperature may be lower than 40°.

The stacks are opened after the lapse of 30 or 35 days when horse dung is used, or after 6 or 7 weeks when spent tan is employed. Since a favourable result depends very much upon the maintenance of a uniform temperature, this is provided for by means of double walls and other arrangements, or even by warming the stacks, as in Carinthia and Styria, where there are very extensive white lead and litharge works. The bent leaden plates are there hung upon lathes, in well-pitched wooden boxes, at the bottom of which the vinegar is placed and mixed with the decomposing materials, such as wine lees, fruit, etc., so that the lead plates do not come into contact with them. After packing, the boxes are closed with lids. A number of boxes of this kind are placed together in chambers which are well closed, and furnished with double walls, the space between which is filled in with some bad conductor of heat, and the chambers are gradually warmed by hot-air pipes, so that after the first week the temperature is not more than 25°, after the second week 37°, after the third week 44°, and after the fourth or sixth week 50°. Then, after a few days, air is admitted to the chambers, and the corroded lead is removed. The process which takes place in these chambers is exactly the same as in the stack method above described.

The white lead thus produced is in an extremely minute state of division, and free from crystalline particles, and in this respect it differs from the substance obtained from solutions of lead salts by precipitation with carbonic acid. This precipitate is generally crystalline in structure, and when used as paint it does not cover the surface to which it is applied so well as the white lead prepared by the Dutch method. The opaque character of this material, technically expressed by the term body, is mainly due to its amorphous structure and the very fine state of subdivision.

The lead plates when taken out are covered with a coating of crude white lead, but are seldom entirely converted into white lead; when this is the case, the product is sold as flake white. To separate the white lead from the unaltered metal, the plates are tapped with the hand, an operation which is very injurious to the health of the workmen; for which reason, this is done immediately upon the removal of the plates from the chambers, while they are still moist, and in all cases with very great precaution.

In some works more regard is paid to the health of the workmen, and mechanical contrivances are used for removing the white lead. An arrangement of the kind is

represented by fig. 284. *bc* is a pulley by means of which the corroded lead plates are hauled up in baskets into an upper chamber, where a workman spreads them upon an endless cloth (*df*), which passes them between a couple of pairs of flanged bronze cylinders (*ff'*), by which means the white lead is rubbed off and falls over the sloping shelf (*i*) into a vessel (*j*) filled with water, while the unaltered lead falls into the box (*h*).

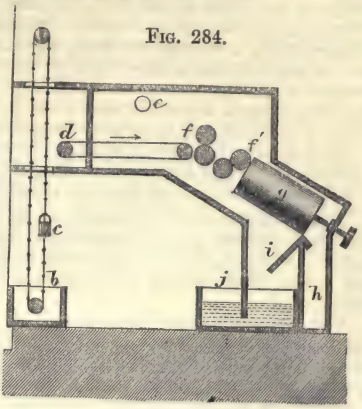


Fig. 284.

Before white lead is fit for use it requires to be ground to a homogeneous impalpable powder. On account of the poisonous nature of the substance, and the danger of injury to the workmen that would arise from grinding it in a dry state, water is always mixed with the white lead in this operation. The mills used for the purpose consist of flat stones running horizontally, and several of them are placed side by side, as shown in fig. 286, which represents a series of nine mills.

Fig. 285 represents a mill of the kind in section; *a* is the shaft with driving

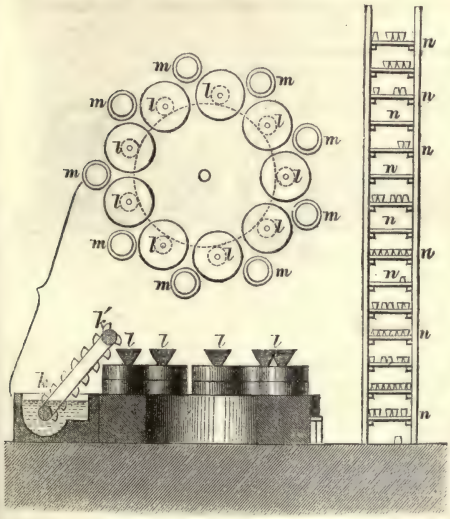


Fig. 286.

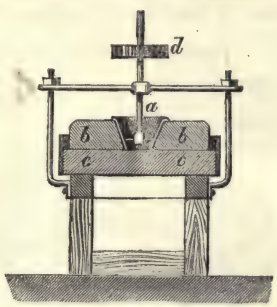


Fig. 285.

gear (*d*), *bb* the runner, *cc* the bed stone. The white lead mixed with water is placed in the cistern (*k*), and then raised by the elevator (*k'*) into the first of the 9 grinding mills (*ll*, fig. 286), from which it is discharged into the receivers (*m m*), and then transferred to the remaining mills successively. After having passed through 7 mills (2 mills being always out of use for cleaning), the white lead is reduced to a very fine paste, and when it has settled it is transferred to unglazed conically shaped pots, having a capacity of 1 to 6 pints, which are first set to dry upon the stand (*n*, fig. 286) in the open air, and afterwards put in a drying chamber. During the drying the temperature must be gradually raised, and care must be taken to avoid sudden change of temperature, since this is apt to make the lumps of white lead split.

White lead is sometimes mixed with a little indigo to increase its whiteness, and after the grinding, gum or dextrin is sometimes added to give it greater density. Hardness is given by the addition of 8 or 10 per cent. of dissolved sugar of lead (lead acetate). It is chiefly the better sorts of white lead that are treated in this way.

White lead is often met with in commerce in the form of cones, weighing from 2 to 3½ lbs. each. If this particular form is not in request, both space and time may be spared by drying the white lead in cakes.

Instead of obtaining the carbonic acid required in making white lead by the fermentation of dung or tan, it may be prepared by combustion of some carbonaceous material, and passed, together with acetic acid vapour and air, into the chambers con-

taining the lead plates. Brammer recommends the use of chambers 24 feet long, 12 feet wide, and 8 feet high, furnished internally with 3 tiers of frames, upon which strips of lead 30 to 40 inches long and 4 inches wide are hung. On the floor is hung a vinegar pot or cauldron, furnished with a steam-jacket for heating it. Carbonic acid is obtained by burning charcoal, and is forced by means of an air-pump through purifiers, to separate dust, into a reservoir, from which it is passed through tubes into the bottom of the white lead chambers, near the vinegar pot. A separate furnace for producing carbonic acid is required for every 4 or 6 chambers. The supply of vinegar vapour is regulated by the steam passed into the jacket, and the supply of carbonic acid by means of stopcocks.

Each of the chambers above described is usually worked in the way described 3 times a day, for an hour, and at intervals of 3 or 4 hours, the complete conversion of the lead into white lead requiring about 30 days.

French Method.—This consists in passing carbonic acid into a clear solution of basic lead acetate, so as to precipitate basic lead carbonate, and leave neutral lead acetate in solution, which is again converted into basic lead acetate by treating it with lead oxide. This process was suggested by Thénard, and practically carried out by Roard.

The solution of basic lead acetate is prepared by dissolving litharge in wood vinegar and evaporating the solution to 18° B. The carbonic acid required may be obtained either by lime-burning or fermentation, by the action of hydrochloric acid upon limestone, magnesite, etc., or by burning charcoal.

An apparatus for preparing white lead according to the French process is represented by fig. 287. The vat (A), of about 4,500 gallons capacity, serves for dissolving

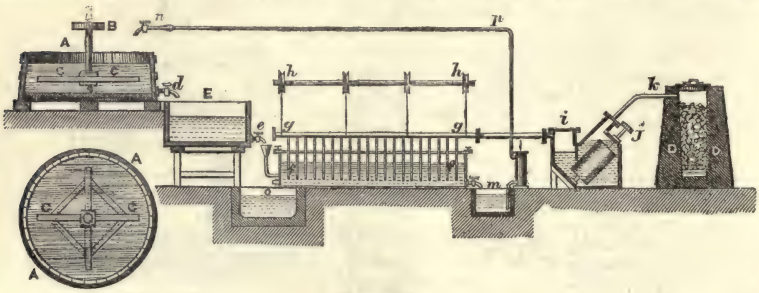


Fig. 287.

the litharge in acetic acid, the solution of the litharge being facilitated by the stirrer (c c); the prepared liquid having a specific gravity of 1·134 is run through the cock (*d*) into the reservoir (E), 5 feet deep, made of tinned copper, where the insoluble substances, such as metallic lead, copper, iron, and sometimes traces of silver chloride, are allowed to deposit, and the clear liquid is then run into a second tank having at a depth of 2 feet a capacity of nearly 2,000 gallons.

This tank is covered with a close-fitting lid secured by clamps. Into the lid are soldered 800 tubes which dip 12 inches into the liquid and are connected with 20 tubes above the lid which branch out from a main (*g g*). Chalk or limestone is burnt with coke (2½ parts limestone to 1 part coke) in a small limekiln (D D), 6½ feet high and 27 inches in diameter at the widest part, which is charged six times daily. The carbonic acid is drawn out through the tube (*k*) by an archimedean screw, then forced into the main (*g g*) and through the 800 branch tubes into the solution of lead acetate. After carbonic acid has been passed in for about 12 or 14 hours the precipitation of the white lead is complete; it is then allowed a few minutes to settle, the clear supernatant liquid—which has then a density of only 5° B.—is drawn off into the tank (*m*), and pumped back through the pipe (*p*) into the solution vat (A) to prepare a fresh quantity of basic lead acetate solution.

The precipitated white lead is then stirred with water, run off from the large tank into the tank (*o*), and after settling there the supernatant liquid is transferred into the vat (A), together with the first solution. The precipitated white lead is washed twice with fresh water and filled into the ordinary moulds to dry.

Instead of dissolving the litharge by stirring it with the sugar of lead solution, it is a simpler plan to filter the solution through litharge contained in tinned copper cylinders.

White lead prepared according to the French method has essentially the same composition as that prepared by the Dutch method, provided excess of carbonic acid

is avoided in the precipitation, which would give rise to the formation of some neutral lead carbonate.

French white lead is superior in whiteness to the Dutch, which generally contains some lead sulphide; it does not cover so well, on which account Dutch white lead is preferred. The difference in covering power of these two sorts of white lead is probably due to the fact that the French variety is crystalline by reason of its formation from solutions at the ordinary temperature, while the Dutch white lead, prepared in the dry way and at a higher temperature, is amorphous. In point of fact, it has been ascertained that, by precipitating a hot solution of basic lead acetate, white lead is obtained of better covering power than the ordinary white lead.

English Method.—Pure litharge, prepared by oxidising lead free from copper in a reverberatory furnace in a state of fine powder and moistened with a 1 per cent. solution of sugar of lead, is exposed to a stream of carbonic acid. The gas is easily absorbed, and in order to facilitate the action the mass is either stirred about with rakes or is placed in barrels turning upon a hollow axis, through which the carbonic acid is passed into them. In this way basic lead acetate is formed which is decomposed by the carbonic acid, while a further quantity of basic lead salt is formed with the unchanged litharge, and so on.

Several other methods of preparing white lead have been proposed with the object of reducing the time requisite for the operation; but none of them have been sufficiently successful to supersede the Dutch method, which is chiefly practised in the manufacture of white lead.

A compound of lead chloride with the oxide $PbCl_2 + PbO$ was introduced by Pattinson as a substitute for lead carbonate, and prepared by grinding powdered galena with strong hydrochloric acid, and thus converting it into lead chloride, which is dissolved in boiling water for the purpose of separating particles of gangue, undecomposed galena, etc.; the solution is then mixed with lime sufficient to decompose one half of the lead chloride and a precipitate is thus obtained consisting of oxychloride. A similar compound is obtained by decomposing lead chloride with ammonia, or by precipitating basic lead acetate with sodium chloride, its composition being probably represented by the formula $Pb_4H_2Cl_2O_4 = PbCl_2 + 3PbO + H_2O$.

White Lead from Lead Sulphate.—Payen suggested that white lead might be readily prepared from lead sulphate—an abundant and almost worthless by-product of calico printing—by treating it with a solution of ammonium carbonate or sodium carbonate, and grinding the two salts together. When the salts are sufficiently subdivided and mixed, the decomposition takes place almost immediately, soluble ammonium sulphate or sodium sulphate being formed, together with lead carbonate.

In order to render white lead cheaper it is often mixed with lead sulphate, heavy spar, chalk, clay, gypsum, and other substances, which are sometimes added to such an extent that the material does not contain more than 10 per cent. of real white lead.

A recent procedure in preparing white lead consists in kneading the moist white lead as it comes from the wet mills (p. 395) with oil. The oil displaces the water and unites with the white lead, settling to the bottom, while the water swims above, and only requires to be drawn off. By this method of preparing white lead, the injurious effects of lead dust upon the health of the workmen are avoided.

Mixtures of this kind are often met with in commerce under various names, such as Venetian white, Hamburg white, Dutch white, etc., and the relative qualities of these articles as pigments correspond to the proportion of foreign substances mixed with the lead carbonate.

These admixtures admit of ready detection by simply treating the white lead with dilute acetic or nitric acid, heavy spar, lead sulphate, clay, and gypsum remaining undissolved; the solution may contain besides lead nitrate or acetate (dissolved white lead), a salt of lime, and by treating such a solution with excess of caustic potash the lime is precipitated. Another method of testing white lead consists in precipitating the acid solution of the salt with sulphuretted hydrogen and filtering off the lead sulphate, when the filtrate ought not to leave any considerable residue upon evaporation. Small traces of residue, however, may be due to the use of spring water in washing out the white lead.

Uses.—White lead is used almost exclusively as paint, for which purpose it is ground up with linseed or poppy oil. The denser its nature, the less oil is it capable of absorbing. In order to secure intimate mixture, the white lead requires to be in a very finely divided state.

White lead paint dries easily in the air, pure white lead facilitating the drying of the oil. Exposed to air and light, the whiteness of the colour becomes intensified; but when mixed with heavy spar, it assumes a greyish hue. In dark places white lead turns yellow; the Dutch white lead more readily than the French; exposed to the

light a bleaching takes place and the white colour is restored. This yellow coloration of white lead paint may be due to the lighter oil coming to the surface during drying, especially when a dense kind of white lead is used; upon exposure to light the oil is bleached and the white colour of the paint restored.

In places exposed to the action of ammonium sulphide or sulphuretted hydrogen, lead colour turns black, owing to the formation of lead sulphide. The darkening of pictures is said to be in part due to this cause.

White lead is sometimes used as a flux, in making glass and enamel colours; it is also used in the preparation of glazed paper, cards, etc.

LEAD ACETATE.

FORMULA $Pb\ 2(C_2H_3O_2)$. MOLECULAR WEIGHT 325.

History.—This salt was known as early as the thirteenth century as sugar of lead, by which name it is still commonly designated. The basic acetate was known at a still earlier period and is described by Geber; in 1760 a solution of this salt was specially recommended for medical use by a French physician, and hence it has been termed Goulard's extract.

Characters.—Lead acetate is a colourless salt, having a peculiar sweet taste. As usually met with, it resembles sugar in appearance; hence the popular name which it bears. It is soluble in rather more than its weight of cold water, and crystallises with three molecules of water. It is also soluble in alcohol. The crystals effloresce in a dry atmosphere, and by absorbing carbonic dioxide are partially converted into lead carbonate; when gently heated they melt and give off water. The dry salt melts at a higher temperature, and is then decomposed with formation of acetone and other empyreumatic products, leaving a finely divided mixture of metallic lead and carbon, which takes fire on contact with atmospheric air.

When lead oxide in the form of finely powdered litharge is digested with a warm solution of lead acetate, it is dissolved and basic acetates are formed. This solution constitutes the Goulard extract or lead vinegar of pharmacy. It has an alkaline reaction, and readily absorbs carbonic dioxide from the air, becoming turbid by the formation of carbonate; when mixed with solutions containing gum or mucilage, an insoluble compound of these substances with lead oxide is formed. There are two distinct basic acetates containing acetic acid and lead oxide in the proportions indicated by the following formulæ:

$$Pb\ 2(C_2H_3O_2)\ PbO$$
$$Pb\ 2(C_2H_3O_2)\ 2PbO.$$

Preparation.—Lead acetate is made by gradually dissolving litharge in acetic acid until the liquid is but slightly acid; it is then evaporated until it has a density of about 1·500, and run into crystallising vats. The vessels used for the purpose are made either of lead or copper.

Uses.—Lead acetate is largely used in calico printing. It is also sometimes employed in the preparation of other compounds, such as white lead according to the French method, aluminum acetate, and ferric acetate. Both the neutral and the basic lead acetates are used in medicine, and in the laboratory.

COPPER.

Symbol Cu. Atomic Weight 63·4.

History.—This metal has been known from the earliest times, and it appears to have been used for making weapons, tools, and agricultural implements long before iron was applied to these purposes. It was termed *æs cyprium* by the Romans, who obtained it from the island of Cyprus; and this name was ultimately corrupted to *cuprum*. The Greeks obtained copper from Chalcis in Eubœa, and hence called it χαλκός, but both this name and the Roman *æs* appear to have been applied indifferently to copper, bronze, and brass.

Occurrence.—Copper occurs naturally in the metallic state, sometimes in considerable masses; but it is much more abundant in various states of combination, chiefly with sulphur, in the form of cuprous sulphide, Cu_2S, as redruthite or copper glance, and in the form of cupric sulphide, CuS, as covellite or indigo copper. These sulphides also occur combined with other sulphides, as in copper pyrites; the composition of which approximates to the formula $Cu_2S.Fe_2S_3$ or CuS.FeS. Another compound of cuprous sulphide with ferric sulphide, varying in composition, occurs as purple or variegated copper, $3Cu_2S.Fe_2S_3$, and a number of other minerals, such as the varieties of fahl-ore, contain cuprous sulphide associated with sulphides of other metals. Cuprous oxide, Cu_2O, occurs naturally as red copper ore; cupric oxide, CuO, as melaconite or black copper; and in combination with manganous oxide as cuprous manganese, with zinc oxide as aurichalcite, and with lead sulphate as linarite; the carbonate combined with cupric hydrate occurs as malachite and azurite.

Cupric silicate occurs as dioptase, $CuO,SiO_2.H_2O$, and with a larger proportion of water as chrysocolla. Cupric chloride occurs combined with cupric oxide and water as atacamite. Cupric phosphates and arsenates also occur naturally.

The sulphur compounds of copper which constitute the principal ores of this metal occur as veins or lodes in the older rocks, frequently associated with other minerals in such large proportions that the mass contains only a small amount of copper. Besides the copper ores occurring in this way, rocks occur in some localities so highly impregnated with copper as to be available for the extraction of the metal. The copper in these rocks is sometimes in the state of oxide, carbonate, or sulphide; but it is probably always of secondary origin and derived from sulphuretted minerals by a series of slow chemical changes, the first being the formation of cupric sulphate as a result of the oxidising action of the atmosphere upon cuprous sulphides, in consequence of which the water in copper mines is often highly impregnated with cupric sulphate. This salt being soluble in water is dissolved by rain, and the solution filtering through beds of limestone or other rocks containing carbonates, is decomposed with production of cupric carbonate, which is deposited in the rocks where the decomposition takes place. At a high temperature the product of decomposition in such cases might be cupric oxide, and if the strata permeated by the copper solution contained organic substance, the cupric sulphate might be deoxidised and cupric or cuprous sulphide formed as a result of the chemical action. Probably the copper pyrites in the bituminous slate of the Mansfeld district in Saxony has originated in this way.

Copper also occurs very frequently in minute proportions in some meteorites, in iron ores, soils, and mineral water. It has also been detected in sea-weeds, in the red pigment of the wing feathers of the Turaco, and in the blood of some animals.

Characters.—Copper has a characteristic yellowish-red colour; its density varies from 8·910 to 8·950. It is very hard, malleable, and ductile; by hammering or drawing into wire the hardness is increased and the metal becomes brittle, but it can be softened again by heating it to redness and allowing it to cool slowly. The fracture is granular after melting, but after the metal has been hammered it breaks with a fibrous fracture. At a red heat it is so brittle that it can be crushed to powder.

Copper melts at a bright red heat somewhat higher than the melting point of

silver and below the melting point of gold. At the ordinary temperature it does not readily oxidise in dry air, but in contact with a moist atmosphere it gradually becomes coated with a green incrustation consisting partly of cupric carbonate; when heated to redness in atmospheric air, copper readily oxidises and becomes covered with a black scale consisting of cupric oxide. It is scarcely affected by hydrochloric acid or sulphuric acid when dilute, but it dissolves readily in concentrated sulphuric acid with evolution of sulphurous oxide; nitric acid dissolves it readily, even when diluted, nitrous fumes being evolved; and moderately strong acid acts violently upon the metal, but very strong nitric acid does not act upon it at all.

The oxidation of copper is promoted very much by contact with acids when it is exposed to the air, and under these conditions the metal is rapidly corroded and converted into a salt. It is in this way that a green incrustation is formed upon culinary vessels that are not thoroughly cleansed from fat, etc., or in which liquids are allowed to remain exposed to the air.

The presence of very small proportions of arsenic, antimony, bismuth, zinc, or iron in copper renders this metal inferior in malleability and tenacity. The toughness of copper is also very much reduced by the presence of cuprous oxide, which is dissolved by the melted metal generally to the extent of more than 4 per cent. (See Blister Copper.) Melted copper is capable of dissolving as much as 19 per cent. of cuprous oxide.

Preparation.—Though metallic copper occurs naturally in North America and some other localities, comparatively very little of it is turned to account. The ores containing copper in the state of oxide and carbonate are in some instances smelted by themselves, and then the production of metallic copper from them consists chiefly in the reduction of the oxide by smelting with coal and suitable fluxes for the separation of the earthy ingredients of the ore. These ores, however, generally contain some admixture of sulphuretted minerals, and some of the copper in them is not reduced by this treatment to the metallic state, but is obtained as a regulus consisting of cuprous sulphide and ferrous sulphide. Sometimes an addition of iron pyrites is found desirable in order to prevent the slag from retaining copper in the state of silicate.

In most instances the ores consisting either of copper pyrites or some other sulphur compound of copper constitute the chief sources from which copper is obtained. The extraction of the metal from these ores is effected by a series of operations based upon the characters of cuprous sulphide, and upon the fact that copper combines with oxygen less readily than iron does. These operations consist in first separating sulphur from the iron pyrites in the ore by oxidation, and at the same time converting greater part of the iron into the state of oxide; then melting the roasted ore with silicious material so as to convert the oxidised iron into the state of a liquid slag, from which the heavier cuprous sulphide separates by subsidence; lastly, decomposing the cuprous sulphide partly by direct oxidation, and partly by the reaction of the cupric oxide thus formed with the unoxidised sulphide, according to the following equation:

$$Cu_2S + 2CuO = 4Cu + SO_2.$$

It is chiefly in this way that copper is reduced when the operation of smelting is carried out in reverberatory furnaces.

When copper pyrites is roasted at a low red heat, sulphurous oxide is given off, and after some time the mass is eventually converted into a reddish-coloured pulverulent mixture of ferric oxide and cupric oxide. At the commencement some ferrous sulphate and cupric sulphate are formed, but these salts are decomposed at a high temperature.

When a mixture of this kind is smelted in contact with carbonaceous substances and silica, the ferric oxide is reduced to ferrous oxide, which combines with the silica, forming a fusible slag, and the cupric oxide is reduced to the metallic state chiefly by the action of carbonic oxide:

$$CuO + CO = Cu + CO_2.$$

It is in this way that copper is reduced when the operation of smelting is conducted in shaft furnaces, and in the case of rich copper ores containing little impurity the roasted ore might be at once subjected to this treatment.

Copper ores, however, generally contain, in addition to cuprous sulphide and iron pyrites, admixtures of other minerals containing arsenic, antimony, silver, and other substances, which have to be separated either to ensure the purity of the copper, or on account of their intrinsic value, and the treatment to which the ore is subjected varies in each case according to the nature and amount of those substances.

Thus, for instance, in the first operation of roasting the ore by which some of the sulphur is separated and the iron converted into ferric oxide, arsenic and antimony are to some extent driven off as vapour by the direct action of the heat or by oxidation.

But at the same time arsenates and antimonates are formed, which remain in the roasted material, and would in the subsequent smelting operation either give rise to the production of speise, which is an alloy of arsenic and antimony with copper and other metals, or render the copper so impure that it would be unfit for use. For this reason it is not found advantageous to roast copper ore to such an extent that it will yield in the first smelting metallic copper, but only so far that in the first instance the copper is obtained in the state of cuprous sulphide, together with some ferrous sulphide and other sulphides, constituting what is termed coarse metal or crude regulus.

After the ore has been sufficiently roasted, it is melted, together with silicious fluxes, limestone, fluor spar, etc., in contact either with the reducing gases produced in a reverberatory furnace, or with the fuel itself in shaft furnaces. The ferric oxide is thus reduced to ferrous oxide, and combining with the silica of the flux, forms a fusible slag, from which the copper separates in the state of regulus, consisting of cuprous sulphide, ferrous sulphide, and other sulphides. So long as the material operated upon in this way contains more sulphur than is sufficient to form cuprous sulphide with the copper, none of this metal is dissolved by the slag, and even though some copper may have been oxidised in the roasting of the ore, it will be converted into cuprous sulphide by the reaction with ferrous sulphide, which takes place very readily according to the following equation: $Cu_2O + FeS = FeO + Cu_2S$.

The ore regulus or coarse metal, obtained by smelting the roasted ore, is roasted in the same manner as the ore, for the purpose of effecting a further separation of sulphur, arsenic and antimony, as well as the conversion of the iron into ferric oxide. The extent to which this roasting is carried depends upon the character of the ore worked. If it be free from any considerable amount of impurities, the coarse metal may be roasted so far that when smelted it will yield at once metallic copper and only a small proportion of copper regulus. More frequently however, when poor ores are worked, the copper thus obtained would be very impure, and it is requisite to roast the coarse metal only to such an extent that in smelting it the whole of the copper is obtained in the state of cuprous sulphide as a regulus differing from the coarse metal only in containing a larger amount of copper and a smaller amount of arsenic, antimony, or other impurities. In some instances these alternate operations of roasting and smelting are repeated several times before the regulus is obtained in such a condition of purity and concentration that it can be worked for metallic copper.

The water collecting in copper mines and pumped out of them in the course of the working often contains a considerable amount of copper in the state of sulphate, together with ferrous sulphate, these salts being formed by the oxidation of copper pyrites, and in some places this copper is extracted by bringing the water into contact with metallic iron, which precipitates the copper in the form of a finely divided spongy mass. This process is termed cementation.

The extraction of copper from poor ores is also practised in a similar manner by first converting the copper into a soluble salt, and separating it from the earthy and other ingredients of the ore by lixiviation, after which the copper is precipitated by metallic iron. When the copper is in the state of oxide it can be dissolved by dilute acids, provided the other constituents of the ore are not also acted upon by acid; but when the copper is combined with sulphur, it must be rendered soluble either by oxidation and conversion into cupric sulphate, by exposure to the air, or by roasting. The ferrous sulphate formed at the same time by oxidation of ferrous sulphide is readily converted by exposure to the air into a basic ferric sulphate which is insoluble. It is also more readily decomposed by heat than cupric sulphate, and is thus converted into basic ferric salt or ferric oxide.

The copper in ores of this kind is often rendered soluble by converting it into cupric chloride, either by roasting the ore with sodium chloride or by digesting the roasted ore with a solution of ferric chloride.

The roasting of copper ores is sometimes carried out either in heaps constructed in the manner already described at p. 362, or in stalls of the kind represented by fig. 288, where the ore is laid upon layers of brushwood between the walls. Arrangements are sometimes made for condensing the sulphur volatilised in roasting copper ores in this way. If necessary, also, the stalls are covered with a roof to protect the roasting ore from rain or from being too much cooled by the access of atmospheric air. Stalls are often made very much larger than those shown in fig. 288, and capable of containing large quantities of ore, and then they

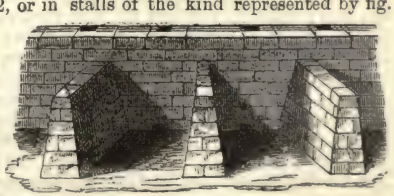


Fig. 288.

are surrounded on all sides by walls in which flues are constructed for the purpose of condensing the sulphur volatilised, as shown in the accompanying drawings (figs. 289, 290, and 291), which represent the stalls used at Agordo, in the Venetian Alps.

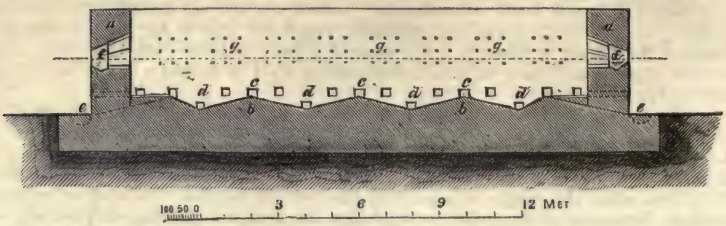


Fig. 289.

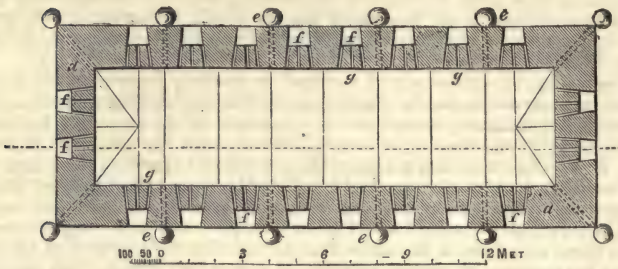


Fig. 290.

The floor of the stall is constructed so as to form ridges (*b b*), communicating at the lowest point with channels (*d d d*) through the walls by which the melted sulphur separated from the ore runs away into receptacles (*e e e*) outside, and the sulphur vapour escapes through the channels (*g g g*) which communicate with the flues (*f f*) where the vapour is condensed. The air requisite for oxidation is admitted through the apertures (*c c c c*) at the lower part of the walls.

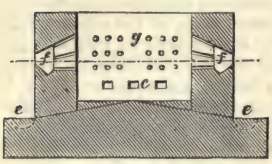


Fig. 291.

Kilns similar to those used for burning lime are also used for roasting copper ores. In all these cases the ore can be roasted in lumps, and as the sulphides, when once sufficiently heated, continue to burn and evolve heat, very little fuel is required. When the ore is in the state of fine powder, it is roasted in a reverberatory furnace.

Ores containing arsenic and antimony in considerable amount require to be thoroughly roasted, and it is often necessary to repeat the operation several times if these substances are to be got rid of in this stage of the treatment. After the ore has been once roasted it is in the subsequent roasting mixed with some fuel to reduce the arsenites and antimonates formed by oxidation. But in any case the ore must not be deprived of the whole of its sulphur, or if there is a deficiency of sulphur in the roasted material some pyrites must be mixed with it when the subsequent operation of smelting is carried out.

In roasting ores containing blende an admixture of coal is requisite for the purpose of decomposing the zinc sulphates formed by oxidation. In smelting a roasted ore containing zinc sulphate this salt would be reduced to sulphide, which is liable to be taken up by the slag. When this is the case, the slag is rendered less fluid, and as it does not readily separate from the regulus, considerable loss of copper is the result.

Ores containing only a very small proportion of copper in the state of sulphide, together with much ferrous sulphide, undergo a remarkable alteration in roasting, the result of which is that the copper accumulates at some point in the interior of the lumps of ore, and while the outer portion of the lumps consists almost entirely of ferric oxide containing only a trace of copper, the core or nucleus consists chiefly of copper combined with sulphur. Advantage is sometimes taken of this fact to concentrate the copper in poor ores by roasting them until the greater part of the ferrous sulphide has been oxidised and the cuprous sulphide has collected in this way at the interior.

The outer part of the lumps is then broken off and the cores are separated. This operation is termed core roasting. It is probable that this concentration of the copper is due to the circumstance that cuprous sulphide is oxidised less readily than ferrous sulphide, so that while a crust of ferric oxide is formed at the outside of the lump of ore, the cuprous sulphide, merely melted by the heat, combines with the unoxidised sulphides at the interior of the lump, and thus gradually accumulates there.

Large quantities of iron pyrites containing about two per cent. of copper are now roasted chiefly for the sake of obtaining the sulphur in the form of sulphurous oxide for the manufacture of sulphuric acid; and since the residue thus obtained, known as burnt pyrites, is afterwards treated for the extraction of the copper it contains, this operation may be regarded as an instance of the roasting of a copper ore.

Spence's furnace for this purpose, already mentioned under the head of Sulphuric Acid (see p. 122), is represented in longitudinal and transverse sections by figs. 292 and 294.

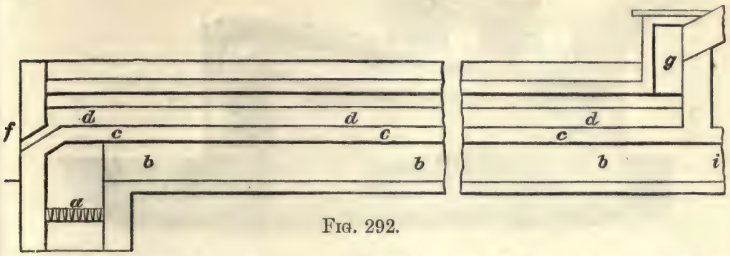


Fig. 292.

It consists of a long bed (*c c c*) constructed of fire brick, in such a manner that it is heated by the flame and hot gas passing from the fireplace (*a*) through the flues (*b b b*), the ends (*i*) of which communicate with a chimney. The finely divided ore is spread upon the bed (*c*) at the end furthest from the fireplace, and when it has become sufficiently hot, it is pushed forwards towards the fireplace by rakes introduced through the doors (e^1 e^2 to e^{12}, fig. 293) at the side of the furnace.

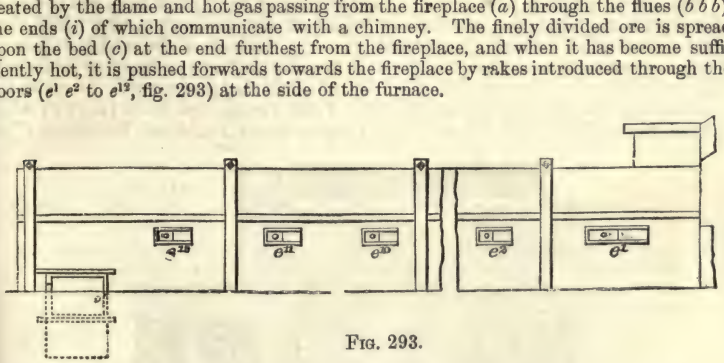


Fig. 293.

The bed (*c*) of the furnace is covered with a brickwork arch so as to form a chamber (*d*), into which atmospheric air gains access through the aperture (*f*) in the brickwork at the end of the furnace, and becomes heated sufficiently in its passage through the chamber (*d*) to oxidise the sulphides on the bed of the furnace.

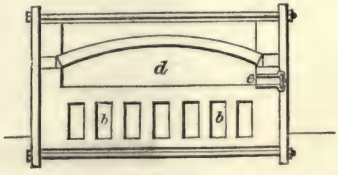


Fig. 294.

Gerstenhofer's kiln, already described at p. 123, is a similar contrivance which is also used for roasting copper ore when it is intended to make use of the sulphurous oxide for the manufacture of sulphuric acid.

In England all the operations involved in copper smelting are conducted in reverberatory furnaces; but on the continent shaft furnaces are very generally employed for the melting and reduction of the ore, the oxidation of the regulus being carried out either in stalls, like those used in roasting the ore, or in reverberatory furnaces, and the term roasting is applied to both of these operations. In this country, however, it is customary to restrict the term roasting to that operation by which metallic copper is obtained from the regulus, which consists chiefly of cuprous sulphide, and is called white metal, and the several operations by which the ore and the regulus are oxidised are termed calcination. In both cases, however, the chemical change pro-

duced consists in the oxidation of the sulphides in the material operated upon, by atmospheric oxygen, and the only peculiarity of the operation termed roasting in this country is, that part of the cuprous sulphide is decomposed by reacting with the cuprous oxide formed at the outset.

Smelting in Reverberatory Furnaces.—The several operations by which copper is extracted from its ores in this way are conducted in the following manner at the smelting works in Wales and Lancashire.

Calcination.—The object of this operation is to effect a partial separation of sulphur from the ore, consisting essentially of a mixture of copper sulphides with iron sulphides; it is conducted in a reverberatory furnace of the kind represented by figs. 295 and 296, in vertical and horizontal sections on the lines x y and z v.

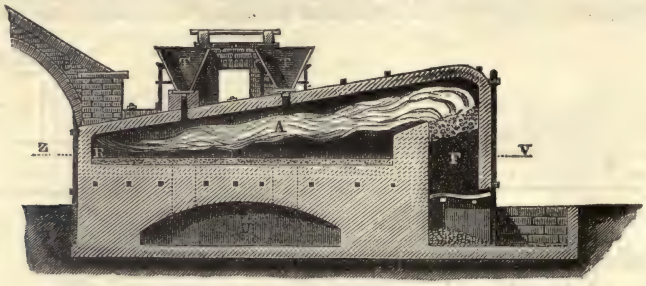


Fig. 295.

The bed or hearth of the furnace is about sixteen or twenty feet long, and is formed of fire brick supported on a solid mass of brickwork over the vault u, with which there is a communication through the apertures (*rrrr*); the roof of the calcining chamber slopes downwards from the fireplace (f) so as to make the flame and gaseous products of combustion come into contact with the charge of ore as they pass towards the smoke flue (rr) leading to a chimney, and at the sides of the furnace are doors (*pppp*) which admit of the ore being stirred from time to time by means of rabbles. The charge of ore

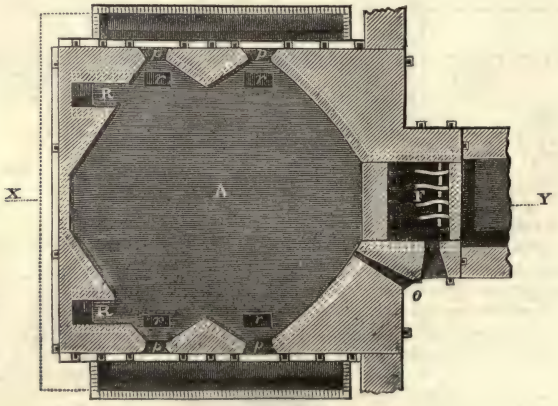


Fig. 296.

is introduced into the furnace by the hoppers (t t), made of cast iron, and then spread evenly over the hearth; and during the calcination the apertures communicating with the vault u are closed by iron plates. A mixture of anthracite and bituminous coal is used as fuel, and a considerable mass of coal is kept upon the fireplace, so that carbonic oxide is at first produced by the combustion, and coming into contact with atmospheric air admitted through the opening (*o*, fig. 296) near the fire bridge, this gas burns with a large flame extending throughout the entire length of the calcination chamber. The ore upon the hearth is thus kept in contact with a highly heated atmosphere of oxidising gas, and a considerable part of the sulphur in the ore is thus converted into sulphurous oxide, which passes away to the chimney, while the greater part of the iron and some of the copper in the ore are at the same time oxidised.

The calcination is generally continued from 12 to 24 hours, the ore being frequently stirred meanwhile so as to expose fresh surfaces to the action of the oxidising gas, and the heat is regulated so as to prevent the ore from caking together during the earlier stage of the operation. When the calcination is completed, the iron plates covering the apertures (*r r*) are removed, and the calcined ore is raked down into the vault (u) and allowed to cool. A fresh charge of ore is then introduced as before by opening the sliding dampers at the bottom of the hoppers, and the operation continued.

The nature of the change which takes place in the calcination of the ore may be seen by the comparison of the figures in the following tabular statement based on the analyses made by Le Play:

Raw Ore.		*Calcined Ore.*	
Cuprous oxide, Cu_2O	0·4		5·4
Copper pyrites	22·7		11·2
Iron pyrites	22·4	Ferrous sulphide	11·2
Various sulphides	1·0		0·6
Ferric oxide	0·6		11·7
Various oxides	0·3		0·6
Silica	34·3		34·3
Earthy ashes	2·0		2·0
Water and carbonic dioxide	0·5		1·1
	84·2		78·1
Atmospheric oxygen consumed	15·8	Water and CO_2	0·5
		Sulphurous oxide	21·4
	100·0		100·0

The loss of weight of the ore by calcination amounts in this operation to about 7·5 per cent., and about 51 per cent. of the total sulphur in the ore is removed. The actual quantity of sulphur thus volatilised chiefly in the state of sulphurous oxide amounts to about 13 per cent. of the weight of ore operated upon, and in the South Wales district several thousand tons of sulphur are thus discharged into the atmosphere in the course of the year. With the object of turning this large quantity of sulphur to account for making sulphuric acid, the kilns already described (pp. 403 and 123) have been introduced in some works for the calcination of copper ores.

It will be seen from the foregoing table that in the roasted ore there is still a considerable proportion of the sulphides left unoxidised, since the object of the subsequent operation of smelting is to obtain the copper not in the metallic state but in combination with sulphur as a regulus, containing a smaller proportion of ferrous sulphide than that originally present in the ore. The sulphur of the ferrous sulphide in the roasted ore is also useful in the smelting as an agent for the reduction of the ferric oxide and converting it into ferrous oxide by the reaction which takes place at a high temperature according to the following equation:

$$\underset{480}{3Fe_2O_3} + \underset{88}{FeS} = \underset{504}{7FeO} + \underset{64}{SO_2}$$

In this way a further separation of sulphur is effected by the formation of sulphurous oxide, and since the ferrous oxide thus produced is capable of combining with silica to form a fusible slag, a considerable portion of the iron may also be separated by adding suitable silicious fluxes to the roasted ore when it is being melted.

If the roasting of the ore be carried too far, part of the copper may be reduced to the metallic state in the smelting by a similar reaction between cuprous sulphide and ferric oxide; but in the presence of a sufficient proportion of ferrous sulphide this does not take place. Under this condition also the presence of some portion of the copper in the roasted ore in the oxidised state, as cuprous oxide or cupric oxide, is not attended with loss of copper in the smelting by the formation of silicate, because the ferrous sulphide in the regulus reacts upon the slag and converts any copper it contains into cuprous sulphide.

If, on the other hand, the ore is insufficiently roasted, the regulus obtained by smelting will contain too large a proportion of ferrous sulphide; consequently the extent to which any particular ore is roasted must be regulated according to the amount of copper it contains. In order to economise fuel in the roasting, the ore should not contain less than 9 per cent. of copper, and to prevent loss of copper in the slag it should not contain more than 14 per cent. Ores of different character in this respect are therefore mixed so that the average amount of copper is about 13 per cent.

Melting the Calcined Ore.—This operation is also conducted in a reverberatory furnace called the ore furnace, which is represented by figs. 297 and 298. The

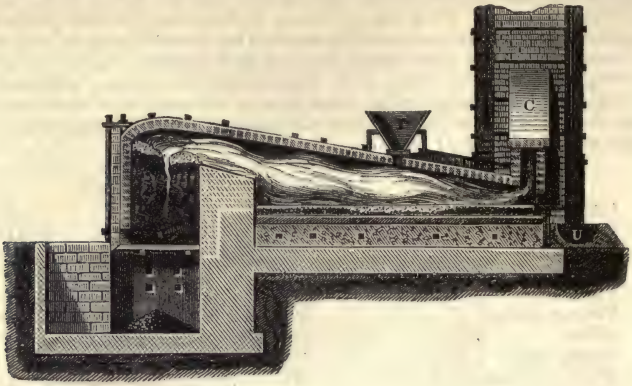


Fig. 297.

bed of this furnace is formed of sand with a hollow at B in which the melted material may collect. The charge consists of a mixture of roasted ore with slag obtained in another operation (see p. 408), and some fluor spar as a flux. It is introduced into the furnace through the hopper (T) and, in melting, the ferric oxide reacts upon the sulphides so as to produce sulphurous oxide, which escapes to the chimney (C), and ferrous oxide, which combines with the silica, forming a fusible slag. At the same time there is obtained a regulus containing the greater part of the copper in the state of sulphide, together with some ferrous sulphide. This regulus collects as it melts in the cavity

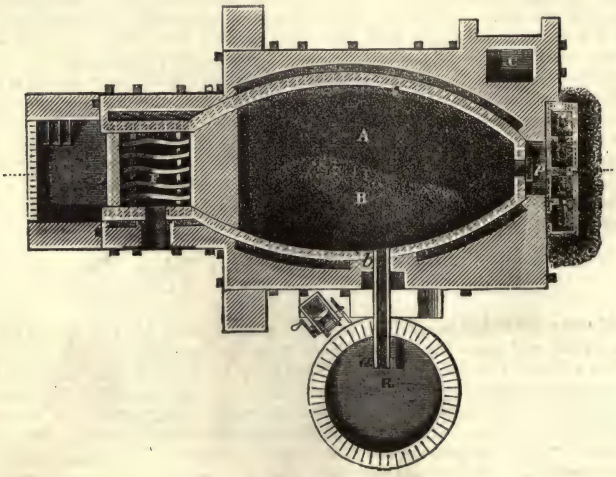


Fig. 298.

of the hearth, and the liquid slag lying over it is drawn off by a rabble through the door (*p*) into the pits (U U) formed in a bed of sand outside the furnace, while the coarse metal is run out through the trough (*b*) into a reservoir (R) containing water so as to reduce it to a granulated condition. The melting operation lasts about 4 or 5 hours.

The regulus obtained by this operation is called coarse metal; it is of a bronze colour, brittle, and easily powdered, and the fracture is granular or vesicular; it generally contains about 33 per cent. of copper, in the state of cuprous sulphide, together with ferrous sulphide, and it has a composition approximating to the formula $Cu_2S,2FeS$, as shown by the following analyses:

	Le Play	Napier		$Cu_2S,2FeS$
Copper	33·7	21·1	39·5	38·0
Iron	33·6	33·2	36·4	33·4
Nickel, cobalt, manganese	1·0	—	—	—
Tin	0·7	—	—	—
Arsenic	0·3	—	—	—
Sulphur	29·2	45·5	25·0	28·6
Slag	1·1	—	—	—
	99·6	99·8	100·9	100·0

The slag produced in this operation is a hard vesicular black glass, with fragments of quartz imbedded in the mass; it consists chiefly of ferrous silicate, the composition of which, as shown below, approximates to the formula $FeOSiO_2$, and the effect of the melting is therefore to separate part of the iron as well as a further portion of the sulphur

	Le Play		$FeOSiO_2$	
Silica		30·0	23·75	45·46
Ferrous oxide		28·5	28·50	54·54
Alumina		2·9	—	—
Lime		2·0	—	—
Magnesia		0·6	—	—
Various oxides (Sn, Mn, Ni, Co)		1·4	—	—
Fluorine	1·0	2·1	—	—
Calcium	1·1			
Copper	0·5			
Iron	0·9	2·0	—	—
Sulphur	0·6			
Quartz fragments		30·5	—	
		100	42·25	100·

The amount of copper in the slag is very small, and it is chiefly in the state of minutely disseminated particles of the regulus. Any copper that may be dissolved in the slag as silicate is converted into sulphide by contact with the ferrous sulphide present in the slag; and to ensure this result iron pyrites is sometimes added in smelting oxidised copper ores.

Calcination of Coarse Metal.—This operation is conducted in a furnace very similar to that in which the crude ore is calcined; free access of air is admitted, and the charge is frequently stirred during the calcination, which lasts from 24 to 36 hours; towards the end of the operation, the temperature is raised to a higher degree than in ore roasting, but not sufficiently to melt the material. Under the influence of atmospheric air, the sulphides are oxidised; part of the sulphur being removed in the form of sulphurous oxide and sulphuric oxide, so that the amount of sulphur in the coarse metal is thus reduced from about 29 to 16 per cent., while oxygen is substituted for it, and both the copper and iron are partly in the state of oxides.

The calcined product amounts to about 97·5 per cent. of the coarse metal operated upon, and the oxidised material is altered in appearance to a brownish-black pulverulent mass, but it is mixed with many hard unaltered granules of coarse metal.

Melting of Calcined Coarse Metal with Oxygenated Materials.—The object of this operation is to separate the iron oxidised in the calcination of the coarse metal as well as that still remaining as sulphide in the roasted material; it is effected partly in the way already described (p. 401), and partly by means of the reaction that takes place between ferrous sulphide and cuprous oxide, ferrous oxide being formed, which is converted into slag, and cuprous sulphide, which separates in the regulus, as represented by the following equation:

$$FeS + Cu_2O = Cu_2S + FeO.$$

The materials added to the calcined coarse metal for this purpose in melting it are almost entirely free from ferrous sulphide, and they should contain, in addition to cupric or cuprous oxides and silicious substances, only cuprous sulphide. Very

little sulphurous oxide is given off, and by mixing these materials together in suitable proportions, the product thus obtained may consist almost entirely of cuprous sulphide. Practically, this is seldom the case, and it has been found preferable to leave a certain amount of ferrous sulphide in the regulus as well as a considerable amount of copper in the oxidised condition in the slag, since slag of this kind is useful in other operations which have for their object the preparation of pure copper.

The regulus obtained in this operation is called fine metal or white metal; when quite free from iron it has a greyish-white colour, and crystalline radiated fracture; its specific gravity is 5·7, and it is quite free from metallic copper. But generally it contains from 4 to 8 per cent. of iron, the colour being darker and bluish, specific gravity 5·3, and particles of metallic copper can be detected in cavities of the mass. In this state it is called blue metal. The composition of the two kinds of regulus is represented by the following figures:

	White Metal	Bluish-white Metal	Blue Metal
Copper	77·4	64·8	56·7
Sulphur	21·0	22·6	23.0
Iron	0·7	9·0	16.3
Nickel, cobalt, manganese	traces	0·5	1·6
Tin and arsenic	0·1	0·7	1·2
Slag and sand	0·3	1·8	0·5
	99·5	99·4	99·3

Cuprous sulphide contains nearly 80 per cent. of copper.

The presence of metallic copper in the blue metal is characteristic of it, and the reduction appears to take place by the reaction of cuprous sulphide with cuprous oxide. When the materials used in this operation contain an excess of copper in an oxidised state, some copper is reduced in this way, and the regulus presents warty excrescences at the surface, on which account it is called pimple metal.

The slag produced in this operation is called metal slag; it is compact, homogeneous, of a dark brownish-green colour, and has a crystalline fracture: the composition varies according as the regulus is free from iron or not.

	Slag from White Metal	Slag from Bluish-white Metal	Slag from Blue Metal
Silica	33·0	33·8	36·0
Ferrous oxide	55·0	56·0	54·4
Cuprous oxide	2·7	0·9	0·7
Other oxides	2·0	2·1	2·5
Alumina	1·6	1·5	0·8
Lime	1·4	1·4	1·2
Magnesia	0·3	0·3	0·2
Copper	2·9	2·9	} 4·2
Iron	0·3	0·3	
Sulphur	0·8	0·8	
	100·	100·	100·

On account of the basic character of this slag, it is used as a flux in smelting silicious ores.

Roasting of White Metal.—The object of this operation is to separate sulphur from the regulus, consisting chiefly of cuprous sulphide, and to obtain the copper in the metallic state. This is effected by exposing the white metal at a temperature near its melting point to the oxidising influence of heated atmospheric air. Part of the cuprous sulphide is thus oxidised, yielding sulphurous oxide, which escapes, and cuprous oxide, which reacts upon the remaining cuprous sulphide, producing metallic copper and sulphurous oxide. At the same time other metals present in small proportions in the white metal are oxidised, and either volatilised or converted into slag by combination with silicious substances.

This operation is conducted in a reverberatory furnace similar to that already described, but furnished with a door at the side through which the pigs of white metal are put into the working chamber, and with openings near the fire bridge for admitting air as it may be required for the oxidation of the cuprous sulphide. While the white metal is being heated sulphurous oxide is given off, as a result of the direct oxidation of cuprous sulphide, and when the charge begins to melt and run down upon the hearth, the cuprous oxide formed by the oxidation reacts with the cuprous sulphide, and the melted mass appears to boil in consequence of the evolution of sulphurous oxide. After several hours, when the whole charge has been melted down, the slag

collecting meanwhile on the surface is skimmed off, and the furnace is allowed to cool down until the melted mass becomes pasty at the surface, and is thrown up in the form of craters by the sulphurous oxide produced within it. During this stage a considerable quantity of cuprous oxide is formed by the oxidation of the partially solidified mass thrown up by the escaping gas and exposed to the air.

After some time the heat is again raised sufficiently to melt the entire charge, and make the cuprous oxide react upon any remaining sulphide. Sometimes materials containing copper in an oxidised state are added with the same object. The slag is then again skimmed off and the metallic copper is run out into moulds.

The **blister copper** obtained by this treatment of the white metal is not perfectly compact, but has numerous cavities throughout its mass, formed by the evolution of gas, the surfaces of the pigs presenting corresponding blister-shaped protuberances; and the fractured surfaces of a pig broken crossways present numerous tubular cavities extending from the bottom to the top of the pig. In this state it has the following composition:

	Le Play	Napier		
Copper	98·4	97·5	98·0	98·5
Iron	0·7	0·7	0·5	0·8
Nickel, cobalt, manganese	0·3	1·0	0·7	—
Tin and arsenic	0·4	0·2	0·3	0·1
Sulphur	0·2	0·6	0·5	0·6
	100·	100·	100·	100·

The slag obtained at the same time, and termed **roaster slag**, is a dark reddish-brown porous mass, consisting chiefly of ferrous silicate together with cuprous oxide, partly in the state of silicate, and metallic copper, as shown by the following analysis:

	Le Play	$FeO, 2SiO_2$ 72 120
Silica	47·5	46·6
Alumina	3·0	—
Cuprous oxide	16·9	—
Ferrous oxide	28·0	28·
Nickel, cobalt, and manganous oxides	0·9	—
Stannous oxide	0·3	—
Lime and magnesia	traces	—
Metallic copper	2·0	—
	98·6	—

On account of the large amount of copper in this slag, it is used as an adjunct in the melting of the calcined coarse metal as already described, and the copper is extracted by the reaction between the cuprous oxide of the slag and the ferrous sulphide remaining unoxidised in the calcined coarse metal.

Blister copper is never in such a condition as to be fit for use until it has undergone further treatment for the purpose of separating impurities and converting the metal into a marketable condition. This is effected partly by the operation of **refining** (see p. 418) in which the foreign metals are oxidised, and partly by the operation of **toughening**, in which the cuprous oxide mixed with the metallic copper is reduced, and the metal is made to assume the requisite texture.

It has already been mentioned that in smelting copper ores containing arsenic, antimony, tin, lead, etc., in any considerable proportion, it is usual to repeat the alternate calcination and melting of the material several times in order to separate these substances either by volatilisation or in the state of slag, before the copper is reduced to the metallic state. In some cases, however, a different plan is adopted, and advantage is taken of the fact that when the copper regulus is calcined so far that in the subsequent melting only a portion of the copper is reduced to the metallic state, almost the whole of the impurities present in the regulus will be concentrated in this reduced copper, while the remaining regulus will by further treatment yield copper of better quality. This operation is termed **selecting**, and it is adopted in producing that kind of copper known as **best selected copper**. The melted material, consisting of a mixture of metallic copper alloyed with the foreign metals and purified regulus, is run into a series of moulds where the copper sinks to the bottom, while the regulus

forms a distinct layer above it. The regulus so purified is termed **close regulus** and the metallic copper is termed **bottoms**. The composition of these products is shown by the following analyses by W. T. Gent and J. A. Phillips.

	Close regulus		Bottoms	
Copper	75·55	75·62	89·63	89·80
Sulphur	19·50	19·60	1·07	0·96
Lead	2·05	2·01	4·75	4·60
Tin	trace	0·06	1·54	1·73
Antimony	trace	trace	trace	trace
Arsenic	0·35	0·28	1·62	1·57
Iron	1·44	1·39	0·30	0·31
Nickel	0·66	0·48	0·76	0·94
Manganese	trace	trace	trace	trace
Alumina	trace	trace	—	—
Silica	0·29	0·25	—	—
	99·84	99·69	99·67	99·91

SMELTING IN SHAFT FURNACES.—In order to effect in this way the separation of copper in the state of cuprous sulphide from the silicious ingredients of the ore and the ferric oxide formed by roasting, it is important to regulate not only the proportion of sulphur to copper in the material operated upon, but also the proportions of silica and ferric oxide, so that a slag may be formed sufficiently fusible to admit of the easy separation of the regulus.

A deficiency of silica has the disadvantage of giving opportunity for the reduction of some iron to the metallic state, and the formation of deposits, consisting chiefly of iron, in the hearth of the furnace. At the same time the regulus produced under these conditions contains too small a proportion of copper and too much iron.

An excess of silica is equally disadvantageous, since it is attended with the formation of slags containing copper as well as iron in the state of silicate, and owing to the more difficult fusibility of the silicates containing a large amount of silica, the smelting operation proceeds but slowly. It is therefore necessary either to mix ores of different composition, or to add suitable fluxes in order that the slag produced in smelting may be sufficiently liquid. In most instances the slags produced in smelting copper ores consist chiefly of ferrous silicate approximating to the formula FeO, SiO_2; but when the ore contains much lime or alumina, the slag must contain a large proportion of silica, and then is probably a mixture of silicates having that composition with others corresponding to $FeO2SiO_2$. In some cases the addition of fluor spar is very useful in smelting ores containing earthy ingredients.

The reduction of the ferrous oxide in smelting roasted copper ore in a shaft furnace is effected almost entirely by the carbonic oxide derived from the fuel. The height of the shaft has considerable influence in this respect, and very ferruginous ores are apt to have some of the iron reduced to the metallic state in furnaces of considerable height, especially when the shaft is constructed without boshes, and the heat generated by combustion produces a much higher temperature in the upper part of the shaft than it does when the width of the shaft is much greater at the part just above the tuyere level than it is either above or below that point. In furnaces constructed with boshes of sufficient width, the heat is more concentrated in the neighbourhood of the tuyeres, and there is less tendency to the production of deposits consisting of iron reduced to the metallic state which solidifies in the hearth.

The shaft furnaces employed in smelting copper ores are generally constructed with an open breast, and the hearth in which the melted products accumulate projects beyond the breast. This form of furnace affords greater opportunity of removing deposits from the hearth than that in which the bottom of the furnace is closed, with the exception of two small holes through which the melted products run off continuously into basin-shaped cavities outside the furnace. In certain cases, however, the closed furnaces have advantages, since they work easier and more rapidly than furnaces with open breast.

In addition to the normal products of slag and regulus, it sometimes happens that in smelting copper ores in shaft furnaces other by-products are obtained, such as the ferruginous deposits already mentioned, and in the case of ores containing much antimony, arsenic, nickel and cobalt, the product termed **speise**, which is an alloy of arsenic or antimony, with varying proportions of iron, nickel, cobalt, copper, and lead: it is less dense than the copper regulus, but denser than the slag, and conse-

quently forms an intermediate layer between them. This product has always a highly crystalline texture, is very brittle and easily fusible. The composition of several samples of the speise obtained in smelting copper ores is given in the following table:

	Hungary			Oeblarn
	Hauch			Schenzl
Copper	12·99	15·52	41·18	48·10
Iron	12·63	75·74	35·41	1·20
Nickel	1·40	—	0·09	0·32
Cobalt	0·09	—	0·04	—
Antimony	60·00	7·36	10·79	21·56
Arsenic	7·42	2·63	6·10	0·76
Sulphur	2·04	trace	2.60	1·88
Lead	0·09	—	0·69	20·69
Bismuth	1·26	—	—	2·04
Silver	0·36	0·03	0·03	trace
Gold	0·06	—	—	—

Speise is sometimes worked for the production of black copper by subjecting to oxidation in a melted state and volatilising the antimony in the state of oxide, but is more frequently concentrated for the production of nickel and cobalt, and when it contains a sufficient amount of silver, this metal is extracted.

The reduction of iron to the metallic state is frequently a source of considerable inconvenience in the smelting of copper ores in shaft furnaces, especially when the temperature is high in the upper part of the shaft and the charge contains too large a proportion of silica. The reduced iron combines with phosphorus, molybdenum, silicon, etc., and is then deposited in the hearth of the furnace, forming a granular mass which gradually blocks it up, and has to be removed from time to time.

The composition of some of the ferruginous products called **bears** is given in the following table:

	Mansfeld	Fahlun	Freiberg	Perm
	Stromeyer	Sefström	Plattner	Caubine
Iron	76·77	64·82	88·51	76·30
Copper	3·40	32·88	—	19·90
Nickel	1·15	—	—	—
Cobalt	3·25	—	—	—
Manganese	0·02	—	—	—
Zinc	—	0·02	—	—
Bismuth	—	—	0·85	—
Vanadium	—	—	—	0·12
Molybdenum	9·97	—	—	—
Arsenic	1·40	—	—	—
Sulphur	2·06	1·20	1·24	trace
Phosphorus	1·25	—	—	—
Silicon	0·35	—	9·03	0·83
Carbon	0·38	—	—	0·73
Alumina	—	0·72	—	—
Silica	—	1·58	—	0·43
Slag	—	—	—	3·33

These products are sometimes smelted with sulphur or iron pyrites, so as to convert them into regulus, from which the copper and other metals can be extracted by the methods adopted with copper regulus. They are also used in smelting lead ores for the decomposition of lead sulphide.

In smelting copper ores in shaft furnaces, other deposits are also formed, consisting of zinc oxide or zinc sulphide, as well as lead sulphide and cuprous sulphide.

The regulus obtained by smelting copper ores in shaft furnaces is roasted either in heaps or stalls, in the same manner as the ore, or, when silver is to be extracted, the roasting of the regulus is conducted in reveberatory furnaces. Regulus containing little antimony or arsenic and a sufficient amount of copper is at once roasted to such an extent that most of the sulphur is oxidised and separated as sulphurous

oxide, and the roasted material, consisting chiefly of oxides, is then ready for the reduction of the copper. When the amount of copper in the regulus is small, and it is associated with considerable proportions of antimony, arsenic, etc., the roasting is only carried so far that on smelting the roasted mass the copper is again obtained in the state of a regulus containing a larger amount of copper. According to the amount of arsenic or antimony present, this operation of concentrating the copper by alternate roasting and smelting, and getting rid at the same time of those impurities, may have to be performed several times in succession. In every case it is desirable to leave a small amount of sulphur in the roasted material that is to be smelted for the reduction of copper, in order to prevent the formation of cuprous silicate that would be retained by the slag.

When the regulus obtained from the smelting contains as much as 60 per cent. and upwards of copper, it will, after roasting, be fit for smelting, but otherwise the concentration treatments must be repeated until this proportion of copper has been reached and the impurities are sufficiently separated. The chief point to be observed is that the roasting should not be carried so far in any case as to admit of copper being reduced to the metallic state in smelting the roasted material. The slag formed in the concentration of regulus consists chiefly of ferrous silicate, together with small quantities of other silicates, and it should not contain more than from one to three per cent. of copper.

The shaft furnaces employed in Sweden for smelting copper ores are of the kind represented by the vertical sections (figs. 299 and 300) taken at right angles to each other. The internal wall (*h h*) is constructed of refractory material, and it is surrounded by a rough wall (*f*) with a space (*g*) between them. The hearth (*a a*) is formed of a mixture of clay and coal dust, beaten down so as to form a cavity extending beyond the breast (*b*) of the furnace. The horizontal section (fig. 301) at the level of the tuyeres (*c c*) shows the shape of the hearth (*a a*) and the position of the tapping hole (*e*) by which the melted contents of the hearth are run off at intervals. In some of the Swedish furnaces the hearth is made of much greater capacity than that shown in the figures, in order to allow of the accumulation of a large quantity of the melted products and give time for the separation of the regulus from the slag.

Fig. 299.

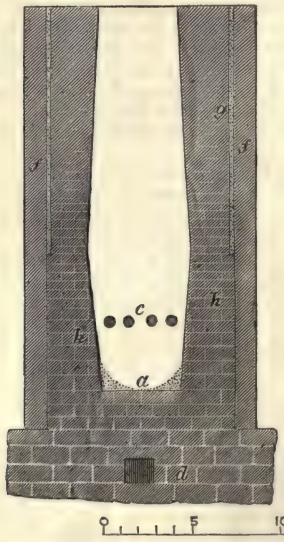
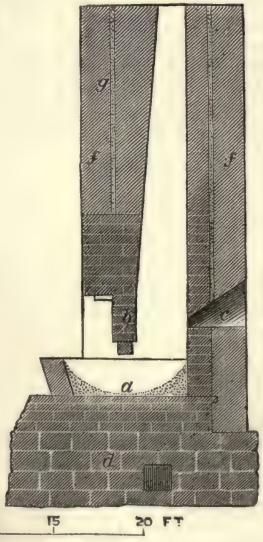
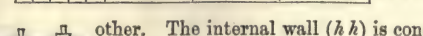


Fig. 300.





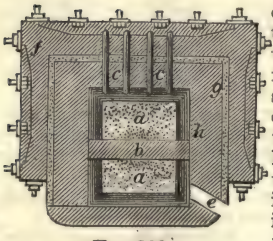


Fig. 301.

The copper ore smelted at Fahlun in Sweden consists of copper pyrites accompanied by iron pyrites and quartz, together with some galena, blende, arsenical pyrites,

and calc spar. The amount of copper in this ore varies from 0·5 to 30 per cent., but averages from 2 to 3 per cent.

After the ore has been roasted it is smelted in a shaft furnace about 18 feet high with an admixture of black copper slag, produced in another stage of the operation, and containing a large amount of ferrous silicate. The proportions of the charge are so adjusted that the slag produced may approximate to the formula $FeOSiO_2$ and contain sufficient silica to prevent the walls of the furnace from being corroded, while at the same time it is liquid enough to facilitate the separation of the regulus. The following table gives analyses of this slag:

	Bredberg	Starbök	Olsen
Silica	44·72	45·35	45·53
Alumina	4·39	3·58	4·22
Ferrous oxide	44·88	43·58	45·61
Lime	3·50	—	—
Magnesia	1·20	7·23	3·50
	98·69	99·74	98·86

The regulus obtained in smelting the ore contains about 10 per cent. of copper and has the composition shown in the following table:

	Bergsten		Winkler	Johnsen
Sulphur	26·35	26·07	26·70	24·62
Copper	8·32	8·85	9·81	12·00
Iron	62·26	60·29	58·14	55·85
Zinc	1·23	1·09	1·44	2·92
Lead	—	traces	0·58	3·96
Silica	0·07	1·78	1·95	0·20
Magnesia	0·44	0·61	—	—
	98·67	98·69	98·62	99·55

The smelting of copper ore is conducted in a similar manner at Näfvequarn, Garpenberg, Atvidaberg, Röraas, and other places in Sweden and Norway; the ore smelted contains a larger amount of copper than that smelted at Fahlun, but as the proportion of blende in the Atvidaberg ore is also much larger, amounting on the average to one third, very careful roasting is necessary in order to convert the zinc sulphide first formed into oxide. In the smelting operation a richer regulus is obtained with from 25 to 30 per cent. of copper.

The regulus is thoroughly roasted in stalls several times in succession, and then smelted, together with quartz or silicious ore, in a shaft furnace of much smaller dimensions than that in which the ore is smelted. The products of this operation are black copper, together with one-fourth as much, or less, of a regulus which is called thin regulus or copper regulus, and a slag consisting of ferrous silicate containing, according to Winkler:

Silica	32·79
Ferrous oxide	66·12
Magnesia	1·58
Copper	traces
	100·49

This slag is used as a flux in smelting the copper ore.

The thin regulus, produced together with black copper, contains, according to Johnsen:—

Sulphur	24·50
Copper	57·78
Iron	17·23
Zinc	0·74
	100·25

It is roasted several times and then smelted, together with the roasted ore regulus.

The black copper contains from 70 to 90 per cent. of copper. A sample from the Atvidaberg works contained---

Copper	94·39
Iron	2·04
Zinc	1·55
Cobalt and nickel	0·63
Tin	0·07
Lead	0·19
Silver	0·11
Sulphur	0·80
Arsenic	traces
	99·78

It is then refined in order to effect the separation of the impurities and the conversion of the metal into a marketable condition. (See p. 418.)

In several parts of Hungary copper ores containing from 0·75 to 13 per cent. of copper are smelted in a manner very similar to that practised in Sweden and Norway. The regulus obtained by smelting the poor ores is roasted and smelted for the purpose of concentrating the copper. The richer ores are smelted at Schmölnitz without being roasted, and a regulus is obtained containing about 20 per cent. of copper.

Ores containing lead and copper, together with silver and gold, such as those in the Naygbanya district in Hungary, are smelted together with lead in order to extract the silver and gold, and as a final product of the operation copper regulus is obtained, which is then either roasted and worked for copper in the usual manner, or smelted with materials containing lead, for the purpose of effecting a further separation of silver, and obtaining a regulus containing a large amount of copper as in the smelting of lead ores (see p. 367). This regulus or the copper regulus obtained as a by-product in smelting cuprous lead ores is roasted and granulated and then treated for extracting the silver, and the desilverised material is smelted for black copper.

At Agordo in the Venetian Alps ores containing on the average 2 per cent. of copper are worked. The poorer ores are submitted to the operation of core roasting, and the ferruginous crust of the roasted lumps is lixiviated to extract any remaining copper. The cores are smelted for regulus in the usual manner.

In the Upper Hartz, and in Silesia, Nassau, and Saxony, copper ores are generally smelted in shaft furnaces, closed at the breast, and furnished with two small apertures at the bottom of the shaft, through which the melted products run out continuously into receptacles outside the furnace.

The ores of the Upper Hartz contain a large amount of antimony, and consequently several alternate roastings and smeltings of the regulus are requisite. The Silesian ores frequently contain a considerable proportion of silver, in which case the regulus is submitted to special treatment for the extraction of this metal.

The cuprous slate smelted at Reichelsdorf and Friedrischshütte in the Grand Duchy of Hesse contains besides sulphuretted and oxygenated compounds of copper, blende, galena, compounds of cobalt, nickel, and other minerals. The amount of copper in the ore is from 3 to 4 per cent. on the average, and it is smelted in shaft furnaces worked with hot blast, the gaseous product being collected at the throat of the furnace and used as fuel for heating the air.

The ore smelted at Mansfeld and the other works in that district is a bituminous shale containing copper pyrites and other sulphuretted minerals, disseminated throughout the mass. The amount of copper varies, and is barely more than 6 per cent., and some of the shale does not contain more than 1·5 per cent., but in some cases there is a considerable amount of silver. The composition of this shale is as follows, according to Berthier :—

Silica	40·0
Alumina	10·7
Ferric oxide	5·0
Calcium carbonate	19·5
Magnesium carbonate	6·5
Copper pyrites	6·0
Potash	2·0
Water and bitumen	10·3
	100·

The shale is first roasted in heaps with layers of brushwood beneath them, and the bitumen it contains serves in part as fuel. Sulphur is driven off as sulphurous

oxide, and some of the iron in the pyrites is oxidised. The burnt shale has a greyish white colour, and has the following composition, according to Berthier :—

Silica	50·6	43·8
Alumina Magnesia	23·4	17·2
Lime	7·8	18·0
Cupric oxide	2·8	2·5
Ferric oxide	9·0	7·2
Sulphur	4·0	2·4
Loss by ignition	0·8	6·0
	98·4	97·1

The roasted ore is mixed with a suitable proportion of fluor spar and smelted to-

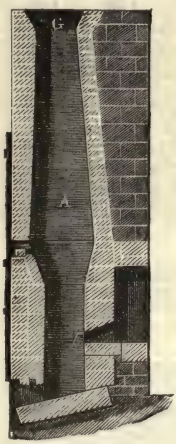


Fig. 302.



Fig. 303.

gether with slags from previous operations in shaft furnaces of the kind represented by figs. 302, 303 and 304. These furnaces are from 16 to 21 feet high and are furnished with two tuyeres (*t t*), and at the bottom of the hearth are two holes (*o o*) through which the melted products are alternately run off into the fore hearths (c c) from which the regulus is taken in cakes as it cools at the surface. Recently, hot blast and much larger furnaces have been used in smelting this slate, and the regulus is run into water for the purpose of obtaining it in a granulated condition.



Fig. 304.

A large quantity of slag is produced, which has the following composition :

	Berthier	Hoffmann		Ebbinghaus	Heine	
Silica	49·8	48·22	50·00	54·13	53·83	57·43
Alumina	12·2	16·35	15·67	10·53	4·43	7·83
Lime	19·2	19·29	20·29	19·41	33·10	23·40
Magnesia	2·4	3·23	4·37	1·79	1·67	0·87
Ferrous oxide	13·2	10·75	8·73	10·83	4·37	7·47
Cuprous oxide	—	0·75	0·67	2·03	0·25	0·30
Zinc oxide	—	1·26	1·11	—	—	—
Fluorine	1·1	—	—	—	2·09	1·97
	97·9	99·85	100·84	98·72	99·74	99·27

The regulus consisting of the metallic contents of the ore in the state of sulphides varies in the amount of copper it contains, as shown in the following table:

	Rammelsberg		Heine			Sontzos
Sulphur	26·76	28·70	26·44	24·58	27·80	32·00
Copper	47·27	43·62	52·44	48·25	31·70	23·58
Iron	19·69	23·35	20·49	17·35	28·75	38·42
Zinc	4·09	3·45	—	2·90	4·35	5·67
Nickel			—	0·80	—	
Cobalt			—		1·25	—
Manganese		—	—	—	—	—
Lead	—	—	0·41	1·05	0·65	—
Silver	—	—	0·13	0·30	0·16	—
Silica	—	—	—	1·55	1·65	—
	97·81	100·	99·91	96·78	96·31	99·67

The regulus which does not contain more than 20 or 30 per cent. of copper was formerly roasted and smelted again in shaft furnaces to obtain a regulus richer in copper and the black copper afterwards obtained by smelting the concentrated regulus was submitted to a process of liquation for extracting the silver it contained. (See p. 431.) This plan has been superseded and the concentration of the poor regulus is now performed in a reverberatory furnace represented by figs. 305, 306, and 307.

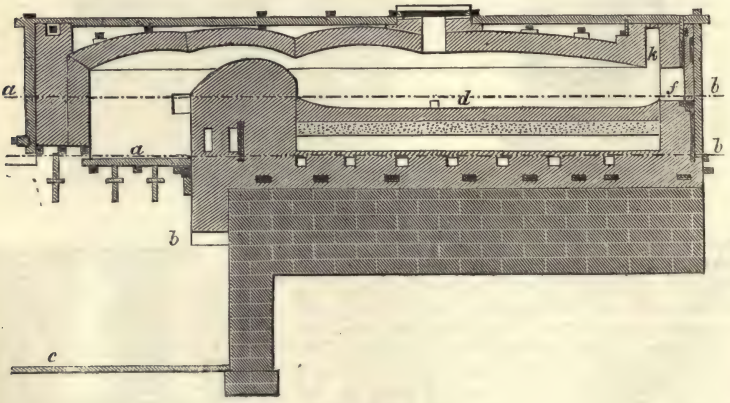


Fig. 305.

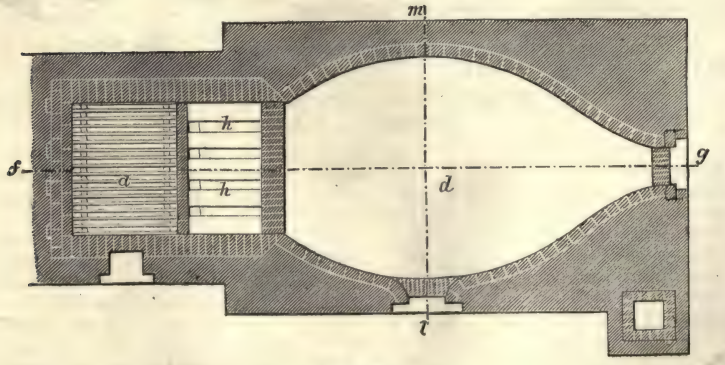


Fig. 306.

The regulus is roasted in muffle furnaces and melted on the hearth (*d*) of the reverberatory furnace mixed with sand or silicious slag, by means of which the ferrous oxide is dissolved and the amount of copper in the regulus increased to about 70 per cent. The slag is then drawn off and the concentrated regulus granulated by running it into water.

Before treating the regulus further for the production of black copper, it is ground to a fine powder and roasted so as to convert the copper into the state of oxide and leave the silver in the state of sulphate. In this condition it is desilverised by Ziervogel's method (see p. 444).

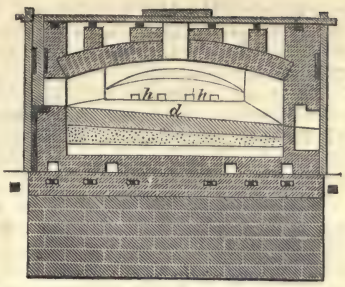


FIG. 307.

The residue from the desilvering of the roasted regulus is then smelted in a shaft furnace to obtain black copper. For this purpose it is mixed with a small quantity of rich regulus to prevent oxide of copper from being taken up by the slag, made into balls with wet clay, dried, and smelted with coke.

In this way the greater part of the copper is obtained in the state of black copper, together with a small quantity of rich regulus, and a slag containing a small quantity of copper, which is used as a flux in smelting ore.

EXTRACTION OF COPPER IN THE WET WAY.—The precipitation of copper from mine water by metallic iron has long been carried out at the copper mines in Wicklow and in the Isle of Anglesea; on the continent mine water is worked in the same manner, at the Rio Tinto mines in Spain, and at Schmöllnitz in Hungary, Rammelsberg in the Hartz, etc.

The treatment of poor cupreous materials with the object of converting the copper into a salt that can be dissolved out by water, is also extensively practised, not only in places where such materials occur naturally, but also in connection with the use of pyrites as a source of sulphur for sulphuric acid factories.

The material operated upon at some places where this method is carried out is a sandstone impregnated with cupric carbonate, and containing on the average about 2 per cent. of copper. The crushed sandstone is mixed with dilute hydrochloric acid in large vats fitted with agitators; the solution of cupric chloride thus obtained is drawn off and the copper precipitated from it by metallic iron.

At Alderly Edge, in Cheshire, a similar plan has been adopted for extracting copper from sandstone.

Sulphuric acid is sometimes used in the same way, for the purpose of extracting copper from poor ores when it exists in an oxidised state: but in either case it is essential to the success of this method that the ore to be operated upon should not contain any large proportion of carbonates which would be decomposed by the acid used and thus consume a large amount of acid. It is also essential that the ore should not contain other substances that would be dissolved by the acid used.

In the case of poor copper ores which contain copper in combination with sulphur, the copper is sometimes converted into sulphate by oxidation, by roasting the ores in heaps and then dissolving out the cupric sulphate by lixiviation with water. This plan has been worked in a rude way at the mines of Rio Tinto and Tharsis in Spain, and other places. In a more perfect manner this plan was applied by Bankart for the treatment of ores, containing a considerable amount of copper, which were roasted in the state of fine powder in reverberatory furnaces. The chief difficulty attending this method of treatment consists in regulating it so that greater part of the ferrous sulphate formed may be decomposed with formation of ferric oxide, and at the same time preventing the decomposition of some of the cupric sulphate formed, and the production of cupric oxide, which is insoluble in water.

The plan that has been found most advantageous for converting the copper into the state of a soluble salt is that of roasting the ore together with sodium chloride. This method of treating copper ores was applied by Longmaid in 1842, and has since been practised with various modifications by others. It is now chiefly adopted for the extraction of copper from the residue left in burning pyrites for the manufacture of sulphuric acid. This material is mixed with from 12 to 15 per cent. of common salt, and if the residual sulphur in the burnt pyrites does not amount to rather more than the quantity of copper in it, sufficient iron pyrites is added to make up the deficiency. The mixture is then roasted in a reverberatory furnace with a long bed. The sulphur of the pyrites is thus oxidised and the sulphuric oxide produced by the decomposition of the ferrous sulphate converts the sodium chloride into sulphate and

hydrochloric acid, which combines with the copper, forming cupric chloride. The formation of cuprous chloride must be avoided by carefully regulating the temperature in the roasting, since the sparing solubility of this substance in water would cause considerable loss of copper.

The roasted mass is then lixiviated with water and a little dilute hydrochloric acid in a series of tanks, and when the solution contains a sufficient amount of copper, it is run into tanks containing a quantity of scrap iron, where the precipitation of the copper is facilitated by heating the liquid. The finely divided copper thus obtained is then washed and melted into ingots.

Refining and Toughening.—The metallic copper obtained by precipitation by iron is always very pure and possesses great malleability and ductility; but that obtained by smelting copper ores either in reverberatory or in shaft furnaces is never in a condition to be used, but contains a variety of impurities, the nature of which depends partly on the kind of ores from which the metal has been produced; among these impurities a small amount of sulphur and some cuprous oxide are always present. The following table gives the composition of some samples of blister copper and black copper:—

	Swansea		Mansfeld	Reichelsdorf	Freiberg	Altenau
	Le Play	Napier	Ebbinghaus	Willie	Lampadius	Hahn
Copper	98·4	97·5	92·83	71·0	69·5	—
Iron	0·7	0·7	1·38	11·0	6·7	0·04
Arsenic	0·4	—	—	—	—	0·45
Tin		1·0	—	—	—	—
Antimony	—					
Lead	—	—	2·79	—	6·0	6·84
Bismuth	—	—	—	—	1·0	—
Silver	—	—	0·26	—	0·5	—
Zinc	—	—			2·0	—
Nickel	0·3	—	1·05	10·0	8·3	0·99
Cobalt		—			1·3	0 04
Sulphur	0·2	0·2	1·07	7·0	trace	—
Oxygen	—	0·6	—	—	—	—
	100·	100·	—	—	—	—

The refining of blister copper is carried out in this country in reverberatory furnaces similar in construction to the smelting furnaces, but without any opening in the roof. The hearth slopes from all sides, and the lowest part is near the door at one end. About six or eight tons of copper are placed upon the hearth, and when melted the metal is exposed for several hours to the oxidising action of the atmospheric air entering the furnace. The superficial oxidation of the cakes of metal while melting furnishes material for the formation of slag by combination of the oxide with the sand adhering to the copper and with the silicious material of the hearth. Arsenic, tin, and other metals which are oxidised more readily than copper are separated by the action of the slag upon them and the remaining sulphur in the metal is separated as sulphurous oxide. To facilitate this action the contents of the furnace are several times stirred, and when the purification of the metal is sufficiently advanced the slag is skimmed off the surface.

The slag formed in the refining of blister copper contains a large amount of copper as well as those metals which the operation is intended to remove, as shown by the following analysis:

Silica	47·4
Alumina	2·0
Cuprous oxide	36·2
Ferrous oxide	3·1
Nickel and manganous oxide	0·4
Stannous oxide	0·2
Lime	1·0
Magnesia	0·2
Metallic copper	9·0
	99·5

This slag is called refinery slag, and it is worked up in the melting of calcined coarse metal as already mentioned.

The copper is then in the state of dry copper and contains cuprous oxide dissolved in it, which renders it deficient in toughness and malleability. The separation of this oxide is effected by throwing upon the surface a quantity of coal and after some time stirring the metal with a pole of green wood, which becomes charred by the hot metal and gives off carburetted gases which reduce the cuprous oxide and in escaping cause the metal to boil up. A sample of the metal is then taken out and tested to ascertain whether it is of good quality, or, as it is termed, tough pitch, and when this is the case the surface is skimmed and the metal is ladled out into moulds.

The reverberatory furnace commonly used in Germany for refining copper is represented by figs. 308, 309, and 310. The hearth is made of a mixture of clay and charcoal,

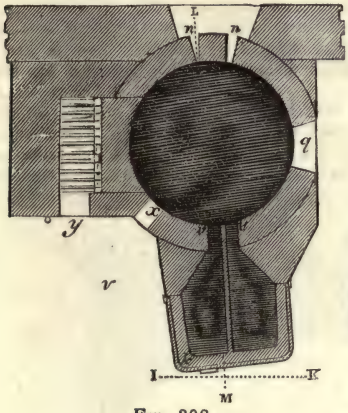


Fig. 308.

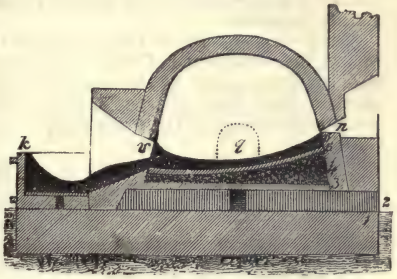


Fig. 309.

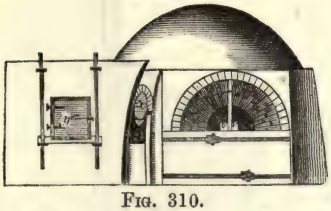


Fig. 310.

and at one side there are two basins (*k*) also lined in the same way, into which the refined metal can be run from the hearth. Fig. 310 is an elevation on the line I K of the horizontal section, showing the fireplace (*y*), the tuyere holes (*n n*), the door (*x*) by which the slag floating on the melted metal is raked out, and the tapping holes (*v v*) which are opened when the refined metal is run out. Fig. 309 is a vertical section on the line L M through one of the tuyere holes, and showing the charging door (*q*).

In some parts of the continent the refining of black copper is carried out in a hearth of the kind represented by figs. 311 and 312. It consists of an hemispherical-shaped cavity (C), formed by compressing a mixture of clay and sand into the space left for it in the brickwork of the hearth, which is constructed so as to leave on one



Fig. 311.

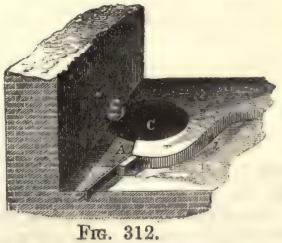


Fig. 312.

side an opening (A), which can be closed by the iron door (*s*). The small channel (*i i*) serves to let the slag run off on to the iron slab (B) with which part of the brickwork is covered. The blast tuyere (T) passes through an aperture (*c*) in the back wall of the hearth.

In working this hearth the copper is placed on the top of some ignited charcoal and melted down with the aid of the blast. In this way iron, lead, and other foreign

metals are oxidised as the copper melts, and the oxides combine with the ashes of the charcoal, and the silicious material of the hearth, forming a fusible black slag. Some copper is also oxidised, and the cuprous oxide dissolving in the melted copper, is again reduced by the cuprous sulphide and by the foreign metals it contains. When these have been almost entirely separated, some of the cuprous oxide remains dissolved in the melted copper, and some of it is dissolved by the slag, communicating to it a reddish colour.

The progress of the operation is tested from time to time by plunging an iron rod into the melted copper so as to withdraw a portion; this is cooled in water and the copper examined as to its flexibility. When the requisite degree of purity has been attained the blast is stopped, the slag and fuel drawn off the surface of the melted metal, and some water thrown upon it sufficient to solidify the upper portion, which is then removed in the form of a thin disc called a rosette. This is continued till nearly all the copper is removed from the hearth.

When copper is refined in hearths it is obtained in the dry state, which is caused by the presence of cuprous oxide, and the toughening of the rosette copper is carried out in a separate operation by melting the metal under charcoal in a hearth like that already described.

At the copper works of Hettestädt a gas reverberatory furnace is used for refining copper, the construction of which is represented by figs. 313 and 314. The combustible gas is generated in the chamber (*a*) which is supplied with fuel through the shaft (*c*) closed by a lid (*d*) at the top. The gas passes into the working chamber over the fire bridge (*f*) in which there is an opening (*g*) for cooling it. Air for com-

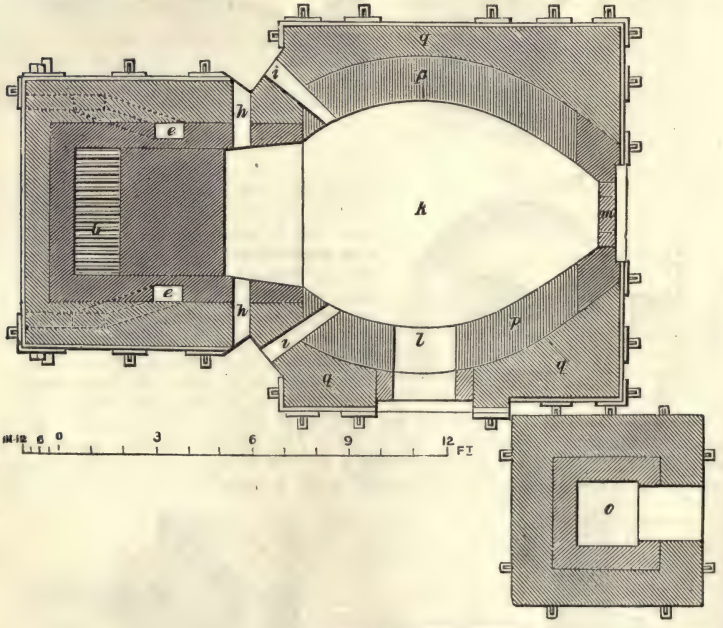


Fig. 313.

bustion is supplied through the flues (*e e*), and if requisite also through the openings (*h h*); the air for the oxidation of the copper is supplied through the openings (*i i*). The door (*l*) at the side of the working chamber serves to introduce the charge, and the working door (*m*) is at the end where the flue (*n*) communicates with a high chimney (*o*) adjoining the furnace. The bed (*k*) of the working chamber is formed of slag and crushed quartz, and the sides (*p*) are lined with a refractory mixture of quartz and loam in order to protect the outer wall (*q q*) of the furnace.

This furnace is capable of working five tons of copper at once.

The slag produced in refining black copper consists partly of silicates and partly of metallic oxides, as shown by the following analyses:

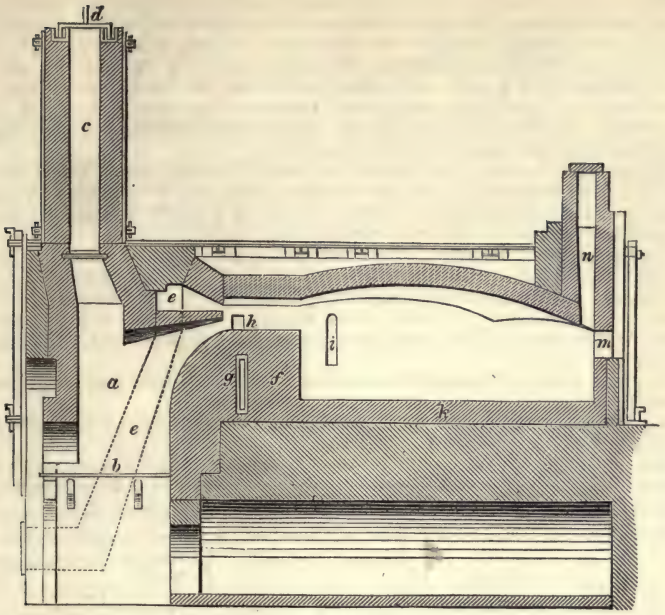


FIG. 314.

	Karsten	Plattner	Genth	
Silica	22·9	4·27	7·88	32·23
Lead oxide	62·1	37·83	—	—
Cuprous oxide	10·4	13·13	1·26	4·79
Ferrous oxide	1·1	2·30	82·49	20·72
Manganous oxide	—	0·17	—	—
Nickel oxide	—	31·53	3·59	34·16
Arsenic oxide	—	5·43	—	—
Antimony oxide	—	4·37	—	—
Alumina	3·4	0·93	0·81	5·60
Sulphuric acid	—	·20	—	—
Molybdous oxide	—	—	2·36	0·87
Lime, potash and soda	—	—	2·26	1·66
	99·9	100·16	100·65	100·03

Uses.—Copper is one of those metals which are of very general applicability in the arts; for the construction of pans, stills, tubes, etc.; for sheathing ships, and for culinary vessels; in the state of alloys with other metals it is also applied to a great number of purposes. Some of the saline compounds of copper are used as pigments; for the preservation of wood, and in medicine.

Compounds.—Copper forms two series of compounds, and it is bivalent in the compounds of one series, but apparently univalent in the others. These compounds are termed respectively cupric and cuprous. There are two oxides, cupric oxide CuO, which is a strong base forming stable saline compounds with acid oxides, and cuprous oxide Cu_2O, which is a feeble base, forming only with a few acid oxides saline compounds which are readily converted by oxidation into cupric salts. The chlorides $CuCl_2$ and Cu_2Cl_2, as well as the sulphides CuS and Cu_2S, correspond to the oxides.

Cupric salts have generally a green or blue colour, but some of them are colourless in the anhydrous state; many of them are soluble in water; they have a disagreeable metallic taste and are very poisonous.

The nitrate is a very deliquescent salt, crystallising in blue rhomboidal prisms, the composition of which is represented by the formula $Cu2NO_3.6H_2O$; it is soluble

in alcohol, and is decomposed when moderately heated, yielding a basic salt of a green colour, which gives off the whole of its acid at a higher temperature, leaving pure cupric oxide as a black powder. The carbonates occurring naturally as malachite and azurite, or prepared artificially by mixing solutions of fixed alkaline carbonate with the solution of a cupric salt, are all basic salts; the precipitate obtained from a hot solution has a green colour, and is known as mineral green or green verditer. The arsenite $CuHAsO_3$ is a brilliant green substance, largely used as a pigment under the name of Scheele's green.

Cupric chloride forms green hydrated crystals, the composition of which is represented by the formula $CuCl_2.2H_2O$; this salt is freely soluble in water and alcohol; when heated it loses water and becomes brown; at a higher temperature the salt gives off half its chlorine and is converted into cuprous chloride.

Cupric acetate $Cu2C_2H_3O_2 + H_2O$ forms dark green crystals soluble in 14 parts of cold water and 5 parts of boiling water; the salt is also soluble in alcohol; it is used as a pigment under the name of distilled verdigris. A basic acetate of a bluish-green colour obtained by exposing plates of copper in contact with the husks of grapes to the action of the atmosphere is used as a pigment under the name of verdigris.

Cuprous salts are generally insoluble in water, and they are very unstable, absorbing oxygen readily, and passing into cupric salts.

Copper unites readily with other metals, and several of the alloys of this metal are important in their practical applications.

Zinc and copper can be mixed together in the melted state in almost any proportions, forming a number of alloys known by the names of brass, Muntz's metal, etc., the composition and characters of which are given in the following table:

	Copper	Zinc	Specific gravity	Colour
Similor	90·72	9·28	8·605	reddish yellow
	89·80	10·20	8·607	"
	88·60	11·40	8·633	"
	81·30	12·70	8·587	"
	85·40	14·60	8·591	yellowish red
Bath metal	83·02	16·98	8·451	"
Dutch brass	79·65	20·35	8·448	"
Rolled sheet brass	74·58	25·42	8·397	pale yellow
Ordinary brass	71·43	28·57	—	"
British brass	66·18	33·82	8·299	full yellow
Muntz's sheathing	60·00	40·00	8·200	"
German brass	49·47	50·53	8·230	"
" for watchmakers	32·85	67·15	8·283	deep yellow
	31·52	68·48	7·721	silver white
	30·30	69·70	7·836	"
	29·17	70·83	8·019	silver grey
	28·12	71·88	7·603	
	27·10	79·90	8·058	
	26·24	73·76	7·882	
	25·39	74·61	7·443	
	24·50	75·50	7·449	
White button metal	19·65	80·36	7·371	
	16·36	83·64	6·605	

The characters which are of most importance in brass are the colour, hardness, and capability of forming sharp castings. The malleability of brass depends partly on the temperature at which it is worked, and it is inversely proportionate to the amount of zinc in the alloy.

Muntz's metal is used for coating ships, and is said to keep cleaner than copper, besides being less costly.

Copper, alloyed with a small proportion of zinc, has a paler red colour than pure copper; with a larger proportion of zinc the alloy is yellow. The alloy consisting of equal parts of the metals has the brightest colour. With a still larger proportion of zinc the alloy is white. The ductility of the alloys of copper and zinc is in many cases greater than that of copper, those containing 15·5 and 28·5 per cent. of zinc being the most ductile. Alloys of copper and zinc become hard and brittle when hammered, and consequently require to be annealed frequently in working them.

Lead mixes with melted copper, but the mass readily separates into two layers, the lower one consisting of lead containing some copper, the upper one of copper containing some lead. Even when the melted mass is rapidly cooled, the greater part of the lead may be separated by heating the alloy to the melting point of lead. The mode of separating lead from copper is sometimes practised under the name of liquation (see p. 431).

The ductility of copper is reduced by the presence of a small amount of lead. Copper containing 0·1 per cent. of lead may be used for ordinary purposes, but cannot be rolled into thin sheets or drawn into thin wire. A small proportion of lead renders brass more capable of being worked in the lathe and in some other respects; but when the brass is to be drawn into wire, the presence of lead is injurious.

The alloys of copper with tin, and sometimes other metals, are known as bronze, gun metal, bell metal, speculum metal, etc. The alloy of copper and nickel is known as German silver; these and other alloys of copper will be described under the heads of the several metals which they contain.

CUPROUS OXIDE.

Formula Cu_2O. Molecular Weight 142·8.

History.—The existence of this substance as a distinct compound of copper and oxygen was first ascertained in 1801 by Proust, who described its characters and the mode of preparing it. In the following year Chenevix showed that red copper ore consisted of this oxide.

Occurrence.—Cuprous oxide occurs naturally as red copper ore and as chalcotrichite or copper bloom, and in some cases it is sufficiently abundant to be worked as an ore.

Characters.—In the crystallised state, cuprous oxide forms octahedrons or cubes, slightly translucent, of a fine red colour, sometimes crimson, and considerable lustre. The specific gravity is from 5·85 to 6·15. The artificially prepared oxide is generally pulverulent and the more finely it is divided the brighter is the colour. Cuprous oxide is readily reduced when heated with carbon or in an atmosphere of hydrogen, carbonic oxide, or other reducing gas.

Cuprous oxide is dissolved by hydrochloric acid, forming cuprous chloride, and it is converted into cupric nitrate by nitric acid, but is decomposed by most other acids, with separation of metallic copper and formation of the corresponding cupric salt.

Cuprous oxide in the hydrated state, obtained by adding caustic soda or potash to a solution of cuprous chloride, or by boiling freshly precipitated cupric hydrate with solution of milk sugar, is an orange yellow pulverulent substance, which is readily converted into cupric oxide by exposure to the air. It is rendered anhydrous by a temperature of 360°, but does not assume the red colour till it is heated to a much higher temperature.

CUPRIC OXIDE.

Formula CuO. Molecular Weight 79·4.

History.—The oxidised copper mentioned by Dioscorides and Pliny under the names of *ἄνθος χαλκοῦ* and *flos aeris* were probably mixtures of cupric oxide with some cuprous oxide, as the substances are described as being reddish when powdered, and beyond the opinion that copper might undergo different degrees of calcination, no distinction appears to have been made between the two oxides until the year 1800.

Occurrence.—Cupric oxide occurs abundantly near Lake Superior, and in smaller quantities it is frequently associated with copper ores.

Characters.—The native cupric oxide is sometimes crystalline, and of a dark steel grey colour, the specific gravity varying from 5·952 to 6·25. More frequently it is in compact masses or, like the artificially prepared oxide, a brownish black powder. Crystals consisting of cupric oxide are sometimes found in the furnaces of copper works.

Cupric oxide melts at a full red heat, and in cooling the mass assumes a crystalline texture. It is not decomposed by heat alone, but is easily reduced to the metallic state when heated in contact with carbon, hydrogen, carbonic oxide, or other reducing gases; it dissolves in melted silicates, communicating to the mass a fine green colour; it is also dissolved by melted lead oxide. When cupric oxide is melted with metallic lead it is reduced to cuprous oxide, which dissolves in the lead oxide formed, and when the proportion of lead is large some of the copper is separated in the metallic state.

Cupric oxide is readily dissolved by acids, with which it forms soluble salts; when heated with fatty substances it is also dissolved to some extent, and on this account copper vessels used for cooking purposes require to be kept bright and free from oxide by frequent scouring.

Cupric hydrate, CuH_2O_2, is a greenish-blue pulverulent substance which is converted into anhydrous cupric oxide at a temperature a little above 100° and by boiling with a solution of caustic alkali. The blue verditer of commerce consists chiefly of this substance. Cupric hydrate is readily soluble in solution of ammonia, forming a deep blue liquid which has the property of dissolving cellulose.

Preparation.—Cupric oxide may be prepared in the form of copper scale, by exposing red-hot copper for some time to the action of atmospheric air, or by moderately igniting the carbonate or nitrate. The hydrate is obtained by mixing the solution of a cupric salt with caustic alkali, quickly washing the blue precipitate with cold water and drying it at the ordinary temperature.

CUPROUS SULPHIDE.

Formula Cu_2S. Molecular Weight 158·8.

History.—The art of extracting copper from copper pyrites appears to have been known at a very remote epoch; Dioscorides describes πυρίτης as a kind of stone, from which copper was obtained; but it appears to have been confounded with iron pyrites, and Agricola described copper pyrites and iron pyrites as varieties of the same mineral. The existence of cuprous sulphide as a distinct substance was first established by Proust in 1801.

Occurrence.—Cuprous sulphide occurs naturally as redruthite or copper glance, associated with other minerals containing copper. It also occurs in combination with ferric sulphide very abundantly as copper pyrites, Cu_2S,Fe_2S_3, and as purple copper ore, $3Cu_2S,Fe_2S_3$.

Cuban is another ferruginous compound of cuprous sulphide that occurs naturally. The regulus obtained in smelting copper ores and in the separation of copper from lead ores is a similar compound of cuprous sulphide with ferrous sulphide. Cuprous sulphide also occurs combined with bismuthous sulphide as tannenite, combined with antimonous sulphide as wolfsbergite or antimonial copper ore, Cu_2S, Sb_2S_3, combined with antimonous sulphide and arsenous sulphide as fahl ore or grey copper, of which there are several varieties, containing also silver, zinc, copper, iron, and mercury, as sulphides in variable proportions. A similar compound of cuprous sulphide and lead sulphide with antimonous sulphide occurs as bournonite, $Cu_2S,Sb_2S_3,2PbS,Sb_2S_3$.

Characters.—Cuprous sulphide, as it occurs naturally, is sometimes in the form of six-sided prismatic crystals, sometimes compact and granular; it has a grey colour, metallic lustre, and the specific gravity is from 5·5 to 5·8. Artificially prepared it has a density of 5·98, a dark lead grey colour, and it melts more readily than copper. It is not decomposed when heated out of contact with air; heated in the presence of air it is oxidised, sulphurous oxide is given off, and cuprous oxide is at first formed, together with some cupric sulphate which is decomposed by further heating. The cuprous oxide is converted into cupric oxide, partly by the sulphuric oxide given off, and partly by atmospheric oxygen. If the oxidation be interrupted before the whole of the cuprous sulphide is oxidised, and the mass be heated sufficiently to melt it, a reaction takes place between the cupric oxide and the remaining sulphide, which results in the production of metallic copper and sulphurous oxide, according to the following equation:

$$2CuO + Cu_2S = 4Cu + SO_2.$$

The same reaction takes place when the mass containing cupric sulphate is melted together with carbon, the cupric sulphate being thus reduced to cuprous sulphide. It is upon this reaction that the production of copper depends in copper smelting. If the proportion of cupric oxide be large, cuprous oxide is produced in place of metallic copper, as shown by the following equation:

$$6CuO + Cu_2S = 4Cu_2O + SO_2;$$

and it is in this way that it sometimes happens that cuprous oxide is produced instead of copper in the smelting operation.

Cuprous sulphide is not decomposed when melted with metallic lead, but if argentic sulphide be also mixed with the cuprous sulphide, the silver is extracted to a great extent by the lead and lead sulphide is formed. Cuprous sulphide mixes readily with lead oxide when they are melted together, sulphurous oxide is given off, some lead

is reduced, and a reddish coloured vitreous mass formed, consisting of lead oxide and cuprous oxide, as shown by the following equation:

$$\underset{158{\cdot}8}{Cu_2S} + \underset{669}{3PbO} = \underset{621}{3Pb} + \underset{142{\cdot}8}{Cu_2O} + \underset{64}{SO_2}$$

But unless the lead oxide amounts to 25 times as much as the cuprous sulphide, a portion of the latter remains undecomposed. If the cuprous sulphide be mixed with argentic sulphide, the silver is taken up by the reduced lead.

Cuprous sulphide is decomposed by metallic iron, yielding a regulus consisting of ferrous sulphide and cuprous sulphide, with brittle copper containing some iron; part of the copper is taken up by the excess of iron.

CUPRIC SULPHIDE.

Formula CuS. Molecular Weight 95·4.

Occurrence.—This substance occurs naturally as covellite or blue copper ore and associated with other minerals containing copper, but it is comparatively rare.

Characters.—The crystallised cupric sulphide is in the form of soft flexible laminæ, but it occurs more frequently in compact masses, or in some instances as a sooty incrustation; it has a bluish-black colour and a slight resinous lustre; its specific gravity is 3·8. Artificially prepared by precipitation with sulphuretted hydrogen from solutions of cupric salts, it has a brown colour while moist, but becomes almost black with a greenish tinge when dried; it oxidises readily when exposed to the air, and in the moist state is converted into cupric sulphate. By ignition, half the sulphur is driven off, and it is converted into cuprous sulphide; it is dissolved by hot nitric acid, the copper being converted into nitrate, part of the sulphur separated, and part converted into sulphuric acid; heated with concentrated hydrochloric acid, it is slowly converted into cupric chloride with evolution of sulphuretted hydrogen and separation of sulphur. It is slightly soluble in solution of ammonium sulphide but not in sodium sulphide.

CUPRIC SULPHATE.

Formula $CuSO_4$. Molecular Weight 159·4.

History.—It was probably this substance, commonly known as blue vitriol, that Dioscorides described under the name χάλκανθον, but up to a comparatively recent time it was frequently confounded with ferrous sulphate or green vitriol and even with verdigris.

Occurrence.—Cupric sulphate frequently occurs in solution in the water that has penetrated into copper mines, and sometimes crystals of the salt occur where such a solution has evaporated.

Characters.—In the crystallised state, this salt contains 5 molecules of water, and forms large transparent prisms of a deep blue colour. The specific gravity is 2·274. It dissolves in 3·5 times its weight of cold water, and in a smaller proportion of hot water, as shown in the following table by Poggiale:

	Temperature	Crystallised	Anhydrous
100 parts of water at	10°	36·9	20·9
	20°	42·3	23·5
	40° dissolve	56·9	30·3
	80°	118·0	53·1
	100°	203·3	75·3

Cupric sulphate is insoluble in anhydrous alcohol, but is slightly soluble in dilute alcohol. The crystals effloresce and turn white at the surface in a dry atmosphere, and at 100° they give off 4 molecules of water, forming a white powder. A tempera ture of 200° is necessary for separating the fifth molecule of water. The anhydrous salt has a powerful attraction for water, and rapidly absorbs it from the air, reassuming the blue colour; on this account it is used as a dehydrating material in preparing absolute alcohol; it is decomposed at a bright red heat, sulphurous oxide and oxygen being given off, while cupric oxide remains.

Cupric sulphate dissolves in hydrochloric acid, forming a green liquid from which cupric chloride crystallises on evaporation. Both the anhydrous salt and the powdered crystals, absorb hydrochloric acid gas rapidly and with evolution of heat,

forming a deliquescent mass. The anhydrous salt absorbs gaseous ammonia rapidly, forming a blue powder. A solution of cupric sulphate mixed with ammonia in excess forms a deep blue liquid which, by evaporation or the addition of alcohol, yields crystals of a salt having the formula $CuSO_4 4NH_3, H_2O$.

Cupric sulphate combines with ammonium sulphate and the alkaline sulphates, forming definite double salts, the composition of which is represented by the following formulæ:

$$Cu2NH_4.2SO_4 6H_2O$$
$$CuK_2 2SO_4 6H_2O$$
$$CuMgSO_4 14H_2O$$
$$CuNa_2 2SO_4 2H_2O.$$

A solution of cupric sulphate mixed with ferrous sulphate, or the corresponding salts of zinc, magnesium, or nickel, yields crystals consisting of the different sulphates in proportions varying according to the relative amounts in the solutions. The form of these crystals is that of the salt present in largest proportion, and the amount of water of crystallisation in them varies in the same manner.

The salt prepared at Buxweiler under the name of Salzburg vitriol is of this nature and contains ferrous sulphate. At other places salts are produced which consist of mixtures in various proportions of the two sulphates. The salt called Cyprian vitriol, prepared at Chessy near Lyons, is a similar mixture of cupric sulphate with zinc sulphate.

SILVER.

Symbol Ag. Atomic Weight 108.

History.—This metal has been known from the earliest times, and the names given to it in various languages refer to the colour; thus, for instance, the Greek name *ἄργυρος* is derived from *ἀργός* white. The extraction of silver from its ores by means of lead was known at a very remote period, and was the only method employed until amalgamation was adopted in Mexico about the year 1557 by Bartholomy von Medina.

Occurrence.—Silver occurs naturally together with silver ores and sometimes in considerable quantities, but it occurs more frequently in combination with sulphur as argentite; the sulphide also occurs combined with cuprous sulphide as stromeyerite, with antimonous sulphide, arsenous sulphide, and other sulphides as the different varieties of fahl ore and other minerals. Silver also occurs combined with selenium as naumanite, with tellurium as hessite, with chlorine as horn silver, with bromine as bromargyrite, with iodine as iodargyrite, with antimony as discrasite, with mercury as silver amalgam. Galena almost always contains silver, probably in the state of sulphide and in varying proportions, and several other minerals, such as blende, iron pyrites, and some kinds of copper ore, often contain small amounts of silver.

Characters.—This metal is remarkable for its whiteness; it is harder than gold but softer than copper, and when polished it has a lustre almost equal to steel. With the single exception of gold it is the most malleable of the heavy metals, and admits of being beaten out into extremely thin sheets of silver leaf, which are not more than $\frac{1}{100000}$ of an inch thick. Silver is also very ductile, and can be drawn into wire so thin that 400 feet of it weighs only one grain. By hammering and drawing into wire it readily becomes brittle and requires to be frequently annealed during the operation.

Silver has considerable tenacity, and a wire having the diameter of only two millimetres (0·0787 inch) is capable of supporting a strain of nearly 87 kilogrammes (187 lbs.) which is the breaking weight. The specific gravity of silver is 10·5 after being melted; by the operation of coining it is increased to 10·57. The finely divided metal obtained by precipitation from the solution of a silver salt has a specific gravity of 10·62. Silver crystallises in forms belonging to the regular system, generally cubes, but the crystals sometimes present octahedral faces.

Silver is the best known conductor of heat and electricity; the conductivity is reduced by increase of temperature. The specific heat of silver is 0·05701, the latent heat of fusion is 21·07; it melts at a white heat, and the melted metal gives off some vapour at very high temperatures; in the presence of vapour of arsenic, lead or zinc, etc., silver is more readily volatilised.

Silver does not combine with oxygen at the ordinary temperature, or when heated in contact with atmospheric air, but it is oxidised under the influence of the electric discharge, and when in a finely divided condition it is converted into peroxide by ozone. When the metal is heated upon charcoal under a jet of oxygen, it burns with a bluish flame and vapour of silver oxide is given off: when melted in contact with alkaline or earthy silicates, it is oxidised to some extent, and the oxide is dissolved by the silicate; it is also oxidised when heated in a finely divided state with cupric oxide, arsenic, or antimony. Silver is not acted upon when heated in contact with caustic alkalies or alkaline nitrates, and on this account silver crucibles are used in chemical operations with these substances.

Melted silver exposed for some time to contact with atmospheric air absorbs oxygen and holds it in solution until the metal has cooled to near the solidifying point. The gas is then suddenly disengaged, producing a kind of effervescence by which particles of the metal are thrown out of the crucible. Melted silver is capable of absorbing in this way twenty-two times its volume of oxygen gas. The presence of a very small proportion of copper in the melted metal prevents this absorption of oxygen.

Silver combines readily with sulphur and decomposes sulphuretted hydrogen, even at the ordinary temperature becoming covered with a brown or black film of silver sulphide; it also combines readily with selenium, phosphorus and arsenic. With chlorine, bromine, or iodine, silver combines even at the ordinary temperature. Hydrochloric acid has but little action upon the metal, unless it be heated to the boiling point with very finely divided silver; but gaseous hydrochloric acid is decomposed by silver at a red heat with formation of silver chloride; vapours of other chlorides are also decomposed by silver in the same way. Finely divided silver is almost entirely converted into chloride when heated to redness with sodium chloride; but when the metal is in lumps, silver chloride is formed only at the surface of them, unless the sodium chloride be melted so as to dissolve the silver chloride and expose fresh surfaces. When sodium carbonate is mixed with the sodium chloride, the formation of silver chloride is prevented. Aqueous solutions of alkaline chlorides act upon silver and gradually convert it into chloride, which dissolves in the solution, forming a double chloride. Solutions of cupric chloride and other chlorides also convert silver into chloride.

Dilute sulphuric acid does not act upon silver, but strong sulphuric acid is decomposed when heated with the metal, yielding silver sulphate and sulphurous oxide. Nitric acid acts violently upon silver, even at the ordinary temperature, forming silver nitrate, with evolution of nitrous fumes.

Preparation.—Minerals containing a large amount of silver are in most instances so intimately associated with the ores of other metals, that they do not admit of being mechanically separated, and consequently in smelting such ores the silver they contain is extracted in the form of an alloy. The ores of lead, as already mentioned, almost invariably contain some silver, and this is often the case with copper ores. The metallic lead or copper or the copper regulus obtained in smelting these ores contains the whole or greater part of silver, and when the amount of silver is not too small, these products are submitted to special operations for the purpose of extracting the silver.

Ores containing a large amount of silver are sometimes smelted together with metallic lead, litharge, or galena, so as to obtain argentiferous lead, which is then operated upon for the separation of the silver. Argentiferous copper ores, or the regulus obtained by smelting them in the usual way, are also smelted with lead or galena, so as to obtain lead containing greater part of the silver, and a regulus containing most of the copper.

Argentiferous iron pyrites is sometimes smelted, so as obtain a regulus consisting chiefly of ferrous sulphide and containing the silver in the state of sulphide. This is roasted and smelted again to concentrate the silver, until a regulus is obtained, from which the silver can be extracted by melting it with lead.

The extraction of silver from its ores, and from other argentiferous materials produced in metallurgical operations, is also effected by a method termed amalgamation, which is based upon the solubility of silver in mercury. This method is practised largely in America, where the cost of fuel is too great to admit of the ores being smelted. The precise nature of the chemical changes that take place in treating silver ores by this method are not thoroughly understood, and some difference of opinion prevails as to the necessity of converting the silver sulphide into chloride. According to the European system of working silver ores by amalgamation, this is done by roasting the ore together with sodium chloride, and then the silver chloride is decomposed by metallic iron in the presence of mercury, which acts merely as a solvent, the reaction taking place in the following equation:

$$\underset{287}{2AgCl} + \underset{56}{Fe} + Hg = \underset{137}{FeCl_2} + \underset{216}{2AgHg}$$

According to the Mexican system, the ore is treated with a solution of cupric chloride and sodium chloride, and it is the opinion of some that the silver sulphide in the ore is in this way converted into chloride, which is decomposed by the mercury with separation of metallic silver, which is dissolved by the excess of mercury, while part of the mercury is converted into mercurous chloride, as shown by the following equation:

$$\underset{287}{2AgCl} + \underset{400}{2Hg} = \underset{471}{Hg_2Cl_2} + \underset{216}{2Ag}$$

In this case, therefore, the quantity of mercury required would be much larger, since in addition to that necessary for dissolving the silver, a further quantity would be consumed in decomposing the silver chloride.

When silver sulphide is digested with solution of cupric chloride no reaction takes place, but, according to Boussingault, in the presence of sodium chloride the

silver sulphide is slowly decomposed and cuprous chloride is formed, which is dissolved by the excess of sodium chloride; the other products are cupric sulphide and silver chloride, probably according to the following equation:

$$3Ag_2S + 4CuCl_2 = 6AgCl + 2CuCl + 2CuS + S.$$

By a further reaction between the cuprous chloride thus formed and a further quantity of silver sulphide, more silver chloride would be produced together with cuprous sulphide:

$$Ag_2S + 2CuCl = 2AgCl + Cu_2S.$$

This view of the change that takes place in the Mexican amalgamation has been disputed, and the formation of silver chloride has been questioned, since ores containing this substance are said to be especially difficult to work by the amalgamation method. The decomposition of silver sulphide is also considered to take place as a result of the reaction with cupric oxychloride, giving rise to cuprous chloride, sulphuric acid, and metallic silver, according to the following equation:

$$Ag_2S + 3Cu_2Cl_2O = 6CuCl + SO_3 + 2Ag.$$

The ores worked by the amalgamation method in Mexico contain some silver in a metallic state together with sulphide and chloride; they sometimes contain antimony and arsenic, and the gangue substance consists chiefly of quartz, iron pyrites, ferric oxide, and earthy carbonates. After being crushed, the ore is ground very fine with water, in a roughly constructed mill, resembling a porcelain mill. The sludgy mass of ground ore is afterwards placed upon a stone pavement, surrounded with a low circular wall, and allowed to dry until it has the consistence of thin mud; it is then mixed with about 5 per cent. of common salt and well stirred together. Some days afterwards it is mixed with about 1 per cent. of a material called magistral, containing cupric and ferrous sulphates, which is prepared by roasting copper pyrites in a reverberatory furnace; the mass is again well mixed, and some mercury is added, the whole being again thoroughly mixed. Chemical action then commences, and the stirring is repeated every day for two to six weeks. Meanwhile samples of the mass are examined by washing with water, so as to separate the mercury. If this is brilliant and liquid, more magistral must be added, but if it presents a very grey colour, the quantity added has been too large and some lime is added.

When the mercury is found to have dissolved the silver contained in the ore, the mass is washed in small portions with water, and the sludge run into settling tanks where the mercury collects at the bottom and the earthy material is run off. This is continued until the whole mass of ore has been washed, and the amalgam is then collected, pressed in sacks to separate the excess of mercury, and then distilled in iron retorts, by which means the silver is obtained in the form of a porous mass, which is melted and cast into ingots.

The consumption of mercury in treating ores by this method is very considerable, and the loss is said to amount to as much as twice the weight of silver obtained. The extraction of the silver is also incomplete.

In working rich ores, the amalgamation is sometimes effected by grinding them in copper pans with successive additions of magistral, salt and mercury.

The silver ores of the Nevada district are amalgamated by grinding in iron pans with mercury, and sometimes common salt and cupric sulphate. The amalgam is then separated by washing with water and distilled.

Some of the silver ores of this district contain intimate admixtures of galena. Arsenical and antimonial minerals cannot be treated in this way, but are roasted with common salt and treated with mercury by the German method.

The treatment of silver ores by amalgamation according to the European system was formerly practised on a large scale at Freiberg. The ores there worked contain silver sulphide together with arsenous and antimonious sulphides, iron pyrites, blende, etc. They are mixed so that when smelted a regulus is obtained amounting to about 30 per cent. The finely ground ore is then mixed with about 10 per cent. of common salt, and roasted in a reverberatory furnace. The charge is put into the furnace moist, heated gently until it is dry, and stirred to prevent the formation of lumps. As the temperature is raised, vapour is given off containing arsenic and antimony. The oxidation of the iron pyrites then commences, and as heat is thus generated little fuel is required at this stage, which lasts about two hours. After the formation of sulphurous oxide has ceased, the heat is again raised in order to decompose the sulphates that have been formed. During this stage the mass swells up, vapour of chlorides and hydrochloric acid are given off, together with some chlorine, and the silver is converted into chloride. After about half an hour the charge is drawn. It then contains, besides various oxides and the earthy ingredients of the ore, silver chloride, cupric

and ferric chlorides, sodium sulphate, together with other sulphates and unaltered sulphides.

During the roasting some silver is carried off by the vapour, and therefore the furnace is connected with condensing flues. The presence of antimony in the ore increases the loss of silver in this way.

The roasted ore is screened to separate lumps, which are ground, and again roasted with salt. The fine powder is ground in a mill, and reduced to a state of very fine division. It is then put into wooden casks with some water and metallic iron or copper, and by means of machinery fitted to the casks they are made to revolve. In this way the silver chloride is gradually decomposed, and metallic silver separated. After this has been done a quantity of mercury equal to half the weight of the roasted ore is added to the contents of each cask, and the stirring is continued for about twenty hours. Meanwhile the contents of the casks are examined to ascertain whether the proper proportions have been used. The casks are then filled with water, and made to revolve slowly for about two hours, after which time the greater part of the mercury will have separated from the sludgy mass and collected together so that it can be drawn from the casks. It is filtered through bags to separate the excess of mercury, and the amalgam left in the bags is distilled in iron retorts.

The pressed amalgam contains about 85 per cent. of mercury and 10 or 12 per cent. of silver, with varying amounts of copper, lead, antimony, etc. The strained mercury contains about 1 ounce of silver to the hundredweight.

The sludgy mass from which the greater part of the mercury has been separated still contains particles of amalgam and mercury disseminated through it, which are separated by washing off the lighter portion of the mass with water, and treating the heavier portion with some more mercury.

The loss of silver and mercury in this operation is very variable, but it is less than in the Mexican amalgamation. Only a small portion of the mercury is converted into mercurous chloride, and the waste arises chiefly from the mechanical mixture with the finely divided material. The presence of arsenic, lead, and other metals which are easily reduced and amalgamated, augments the waste of mercury very much. Still the loss of silver is much less than when the ores are smelted: the operations are very simple, and very little fuel is required. The amalgamation method, however, is not applicable to ore containing lead or copper. Although lead unites readily with mercury, only a small portion of this metal is amalgamated when ore containing lead is operated upon. This is probably due to the circumstance that the greater part of the lead remains in the state of chloride or sulphate, neither of which are decomposed unless a very large excess of iron is used. Copper is to some extent amalgamated, but the greater part remains in the waste and is lost. Consequently ores containing more than 7 per cent. of lead or 1 per cent. of copper are not suited for treatment by this method.

Auriferous ores cannot be advantageously worked by this method, because the greater part of the gold remains in the waste after amalgamation. The cause of this is that, though gold unites readily with mercury, it is less readily acted upon than the very finely divided silver precipitated by the iron from a solution of silver chloride in sodium chloride.

The nature of the earthy ingredients of the ore has likewise some influence in the working: argillaceous substances render the mass tenacious, heavy spar makes it dense; calcareous substances reduce the consumption of iron and of mercury by decomposing the chlorides, but they also reduce the yield of silver. When copper is used for decomposing the silver chloride a purer amalgam is obtained than when iron is used; but copper acts more slowly than iron, and even when used in large proportion is less effective in extracting the silver.

At Poullaouen in Brittany some of the ores from the Huelgoat mines, consisting of metallic silver, antimonial silver, and silver chloride disseminated through quartz, ochre, and clay, are treated in a manner which combines both the Mexican and European methods. After the mechanical preparation of the ore, it is mixed with about 10 per cent. of a material consisting chiefly of sodium chloride with some ferrous sulphate, alum, and a very small proportion of cupric sulphate. The mixture is left for several days in tubs to allow the chemical action to take place, and then it is treated with mercury in the manner already described.

The amalgamation method is now largely practised in California and Nevada in working silver ores, and great improvements have been made in the mode of operating. Large iron pans are used for grinding the ore with the mercury in place of tubs, and by this means the silver or its compounds are more effectively brought into contact with the mercury. The application of heat in the operation has also been found advantageous in some instances.

The cupric oxychloride is supposed to result from the oxidation of cuprous

chloride, formed in the first instance, together with mercurous chloride, by the action of mercury upon cupric chloride: $2CuCl_2 + 2Hg = Hg_2Cl_2 + 2CuCl$, and then converted into cupric oxychloride by absorbing oxygen from the atmosphere: $2CuCl + O = Cu_2Cl_2O$. According to this view, the action of sodium chloride in the amalgamation of silver ores would probably consist chiefly in dissolving the cupric oxychloride and thus facilitating its action upon the silver sulphide.

The solubility of silver chloride in a strong solution of sodium chloride has also been taken advantage of for the purpose of extracting silver from argentiferous materials. For this purpose the silver is converted into chloride by roasting the material with sodium chloride, and the roasted material is then digested with a solution of salt in wooden vats until the silver chloride is dissolved. The solution is then drawn off and passed through a series of vats containing precipitated copper, which precipitates the silver and is itself dissolved.

A still more simple and inexpensive method of extracting silver from argentiferous copper regulus is based upon the solubility of silver sulphate in water, and the circumstance that this salt requires a higher temperature for decomposition than the other sulphates soluble in water which are produced in roasting copper regulus or argentiferous iron pyrites. The success of this method depends mainly upon the proper roasting of the material from which silver has to be extracted, so that the whole of the silver may be converted into sulphate, while the cupric sulphate and ferrous sulphate produced in the earlier stage of the oxidation are decomposed or converted into an insoluble state. These methods are applicable in the case of silver ores, provided they do not contain much lead, zinc, antimony, or arsenic.

It has already been mentioned that in smelting argentiferous lead ores the silver they contain is taken up by the metallic lead, and the amount of silver in the lead obtained by smelting such ores is frequently sufficient to admit of its being profitably extracted. Argentiferous copper ores, when smelted in the usual way, yield a regulus containing silver, and in some instances the silver is separated from the copper by melting the regulus with metallic lead, or with materials containing lead, much in the same manner that lead ores containing copper are smelted. By this means argentiferous lead is obtained, and a copper regulus containing less silver; but the separation of the silver from the copper regulus is seldom effected completely unless the operation is performed several times, and then there is always considerable loss, as well as great consumption of fuel.

If the argentiferous copper regulus is subjected to the usual treatment for the production of metallic copper, the black copper thus obtained contains the silver, and formerly it was the practice to extract the silver by melting the black copper together with lead, casting the alloy into round cakes, and subjecting them to a heat sufficient to melt lead. This process is termed liquation, and the separation of the silver is due to the circumstance that in cooling the triple alloy of lead, copper, and silver, it separates into two alloys, one consisting of copper and lead, the other of lead and silver. On heating this mechanical mixture, the argentiferous lead separates, in the liquid state, from the less fusible alloy of copper and lead.

The heating of the cakes of alloy was carried out in a kind of hearth, the construction of which is represented by figs 315, 316, and 317.

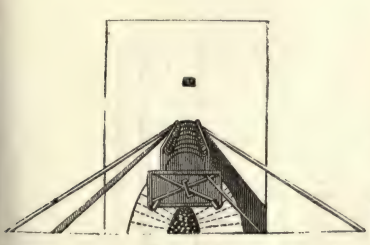


Fig. 315.

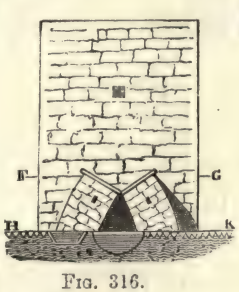


Fig. 316.

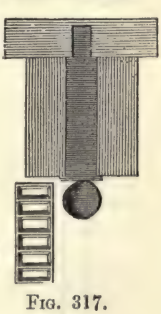


Fig. 317.

It consists of two low walls on the top of which are placed cast-iron plates upon which the cakes of alloy are set on edge with charcoal between them, and a fire is made in the arched space between the walls. The melted argentiferous lead running into the receptacle placed in front of the hearth, is then ladled into moulds. In this way the greater part of the silver is separated from the copper, but there is always a considerable loss of the metal.

The spongy mass remaining still contains lead, and for its separation a higher degree of heat requires to be applied to it, in a furnace of somewhat similar construction, which is termed a sweating furnace. This method of extracting silver from copper was formerly practised on a large scale in Germany, but has now been very generally superseded, and the regulus obtained by smelting argentiferous copper ores is desilverised before the copper is reduced to the metallic state. (See pp. 417, 444.)

The argentiferous lead obtained by the operation of liquation was treated in the same manner as that produced in smelting argentiferous lead ores.

The extraction of silver from argentiferous lead is effected by exposing the melted metal to the oxidising action of heated air; lead oxide is thus formed, which melts and is run off, but the silver is not oxidised to any considerable extent, and ultimately the greater part of it remains in the metallic state. This operation is termed cupellation, and is conducted in a reverberatory furnace with a bed (D, figs. 318 to 320),

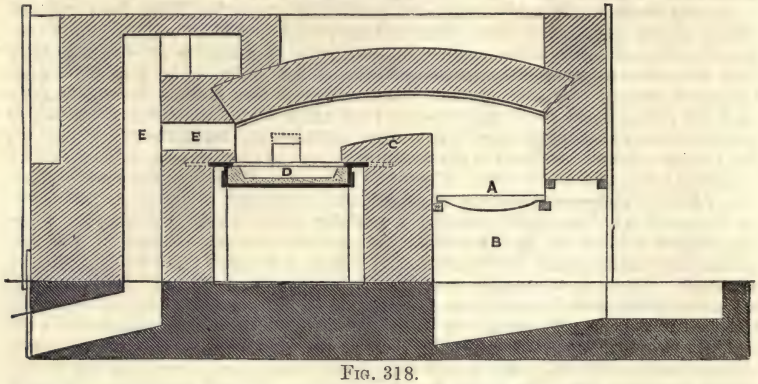


Fig. 318.

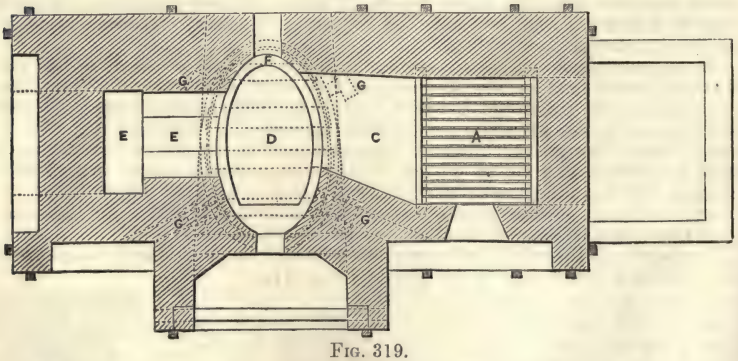


Fig. 319.

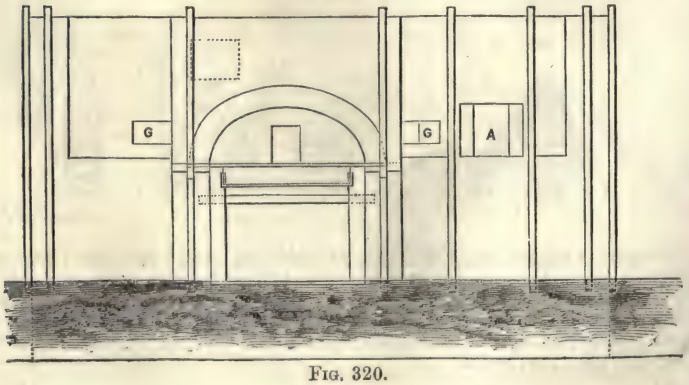


Fig. 320.

formed of bone ash beaten down into a moveable iron framework, represented in the vertical section, fig. 318, by the thick lines, and on a larger scale by fig. 321.

The moveable bed of the English cupellation furnace is called a test. It consists of an oval iron ring (*a a*, fig. 321) with strong iron bars (*b b*) bolted to it, forming the bottom. A mixture of finely ground bone ash, moistened with a very weak solution of potassium carbonate, is beaten down into a compact mass in the cavity of this frame, and then scooped out so as to form a basin (*c*) and leave a lining (*d d d*) which covers the whole of the iron work. The apparatus used in lining the test frame is represented by fig. 322.

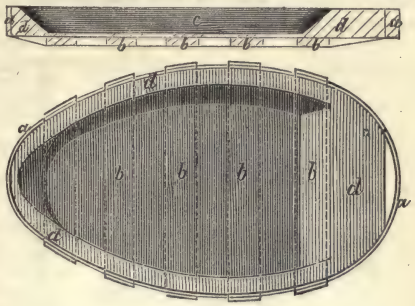


Fig. 321.

At the wider end of the test a portion of the lining is sometimes cut away so as to leave a space between the lining and the ring, through which the melted lead oxide may flow away; but it is now more usual to bore some holes through the lining, and cut a channel in the upper edge of the lining to such a depth as is required.

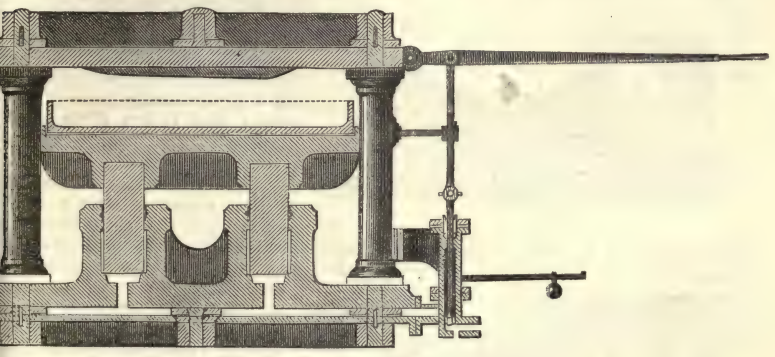


Fig. 322.

The working chamber of the furnace is separated from the fireplace (A) by a wide fire bridge (C), and the hot gas passes over the test (D) through the flues (EE) into the chimney. Opposite the narrow end of the test there is an aperture (F) in the wall of the furnace through which a blast tuyere is inserted, and at the other end of the test a channel is cut in the bone-ash lining of the test, or holes are bored in it, through which the melted lead oxide runs off. The lead from which silver is to be extracted is run into the test from a pot outside the furnace, and while heating up to the requisite temperature, the surface becomes covered with a greyish crust of dross. As soon as the lead oxide melts and the metal becomes visible, the blast of air is turned on to accelerate the oxidation, and the melted litharge is driven off the surface of the metal by the current of air towards the gate or outlet at the opposite end of the test, where it runs out into an iron vessel mounted on wheels. As the metal in the test is reduced in this way, fresh lead is supplied at intervals, either in a melted state or by slipping in pigs of lead through apertures (GG) in the sides of the furnace, so as to keep the test full.

When the operation has been continued so long that the metal in the test is sufficiently rich and contains about 8 per cent. of silver, the furnace is either allowed to cool, and the test removed with its contents, or the metal is run off by drilling a hole in the bottom of the test and running it into moulds.

The further separation of the lead is effected in the same manner upon a fresh test, and the operation is continued until the metal remaining is nearly pure silver. This point is indicated by the brightening of the surface of the metal. The blast is then turned off and the mass of silver, after being allowed to solidify, is removed together with the test.

The proper regulation of the temperature in this operation is of considerable in-

fluence upon the loss of silver and lead. When the heat is too great much lead is volatilised, and when it is too low the melted litharge is viscid and carries off some silver. During the latter stage of the operation the litharge formed contains a larger proportion of silver, and on this account it is kept apart.

The extraction of silver from lead by cupellation is conducted much in the same manner in Germany, but the furnaces employed differ in having the bed fixed, and in

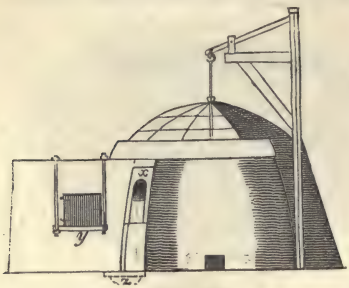


Fig. 323.

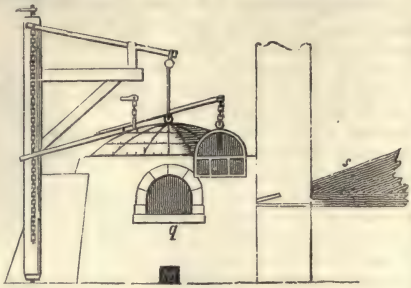


Fig. 324.

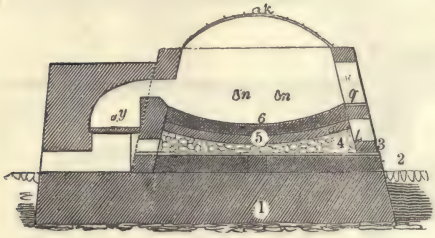


Fig. 325.

being fitted with a movable sheet-iron roof or dome, as shown by figs. 323 to 326.

The hearth (6) of this furnace was formerly made of washed wood ashes mixed with some lime, but is now generally made of calcareous marl beaten down upon the bricks (5), set so as to form a hemispherical cavity; beneath them is a layer of slag (4), and the whole is supported upon a solid foundation (1) with channels (2) for the escape of moisture. The back and front elevations, (figs. 323 and 324) show the position of the working door (q) by which the lead is put in while working, and of the bellows (s), the arrangement by which the dome (k) is taken off; the furnace door (y) and the opening (x) through which the litharge is drawn off into receptacles placed over the pan (z), which serves to collect anything that may be spilt.

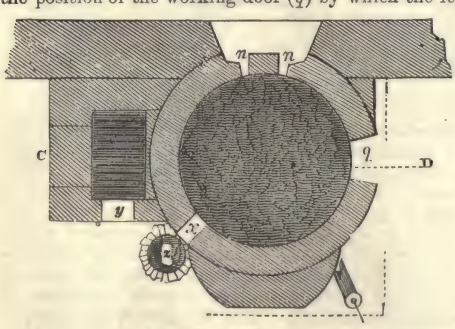


Fig. 326.

In working this furnace the charge consists of from 3 to 5 tons of argentiferous lead. When this is melted down upon the hearth, a pasty dark-coloured scum collects upon the surface, consisting of a mixture of lead with metallic oxides, sulphides, arsenides and antimonides, together with some particles of marl from the hearth. After this scum is raked off, the blast is turned on, and the heat increased, a further quantity of frothy scum is removed, and when the lead oxide formed is sufficiently free from impurities, a notch is cut in the edge of the hearth opposite the door (x), deep enough to allow the liquid litharge to run out. If the lead contains much antimony, the heat must be raised very gradually to ensure the oxidation of the antimony, which is then separated after the removal of the dark frothy scum in the state of lead antimoniate, presenting a greenish-brown colour.

During the operation, the melted litharge should form a ring about fifteen inches wide round this metal, and this is regulated by cutting the notch deeper as the lead is oxidised. The blast should be directed upon the surface of the metal by adjusting the tuyeres ($n\,n$) so as to cause a slight undulation, and drive the melted litharge towards the edges of the hearth. Towards the end of the operation, when but little

lead remains unoxidised, the temperature requires to be increased in order to prevent the metal from solidifying.

The material of which the hearth is made absorbs a large quantity of lead oxide, and often contains from 58 to 65 per cent. of lead with some silver; it is therefore smelted together with lead ores. The actual loss of lead, chiefly by volatilisation, amounts to about 8 per cent., and the loss of silver is about 0·5 to 0·75 per cent. of the quantity in the lead operated upon.

The loss of silver experienced in extracting this metal from argentiferous lead by cupellation is chiefly due to the retention of some silver by the lead oxide. The extent to which this takes place depends very much upon the temperature at which the operation is conducted, and likewise upon the rate at which the melted lead oxide is allowed to flow away. The higher the temperature and the more rapidly the operation is carried on the greater is the proportion of silver carried off in the lead oxide; but the longer the lead oxide remains in contact with the metal the smaller is the loss of silver in this way.

The silver thus obtained is called **brightened silver**; it usually contains about 6 per cent. of impurities, chiefly consisting of lead, copper, bismuth, arsenic and other metals, and the separation of these is effected either by exposing it in a melted state for some length of time to the action of an oxidising atmosphere, or by melting the silver in crucibles with an oxidising flux.

Much of the lead obtained on the continent by smelting in shaft furnaces is very impure, containing copper, zinc, iron, antimony, and arsenic, in considerable proportions, and it is by the oxidation of these metals at the commencement of the cupellation that the dark-coloured scum is produced. In extracting silver from lead of this kind, the entire quantity of lead treated in one operation should be placed on the hearth at once if it be desired to obtain pure litharge as a product, for if the lead were added in successive portions, the impurities it contains would be to a great extent mixed with the whole of the litharge.

The following table gives the composition of the scum formed during the earlier stage of the cupellation.

	Pontgibaud		Poullaouen	Katzenthal	Freiberg	Villefort
Lead	23·0	—	63·6	—	—	—
Lead oxide	53·1	89·5	—	67·6	95·5	82·0
Cupric oxide	1·1	0·2	7·0	0·4	0·5	—
Zinc oxide	4·6	1·5	—	0·2	1·1	—
Ferric oxide	5·4	2·6	28·6	4·4	0·3	—
Antimonic oxide	—	—	—	—	—	17·6
Antimony teroxide	0·5	—	—	—	—	—
Arsenic oxide	3·0	0·7	—	19·2	2·2	—
Sulphur	—	—	—	0·3	—	0·4
Carbon	5·6	—	—	—	—	—
Silica, alumina, etc.	—	—	1·6	7·6	—	—
	96·3	94·5	100·8	99·7	99·6	100·0

It is evident from the composition of the products comprised in the above table, that in extracting silver from lead by cupellation there is at the same time a very considerable separation of the foreign metals with which it is associated. The result is due in some cases to the solvent action of the lead oxide formed during the operation upon the oxides of other metals such as copper, zinc, tin, antimony, etc.

In order to extract silver from argentiferous lead by this method, the lead should not contain less than about 8 ounces of silver in the ton, otherwise the value of the metal obtained is not sufficient to cover the cost of the operation and of the subsequent reduction of the lead oxide produced. A very large proportion, however, of the lead produced contains a much smaller amount of silver, varying from mere traces to 3 or 4 ounces in the ton, and formerly the silver in such poor argentiferous lead was not obtainable, until early in the present century another method was accidentally discovered by Mr. Pattinson, which admitted of much smaller quantities than 8 ounces in the ton of lead being profitably extracted.

When argentiferous lead is melted and allowed to cool gradually, crystals are formed which sink to the bottom and contain much less silver than the metal which remains liquid. Advantage was taken of this fact by Mr. H. L. Pattinson as a means for effecting the separation of silver from lead, and it had the merit of being applicable to lead containing only such amounts of silver as cannot be profitably extracted by

the cupellation method. This method is now extensively employed, and a considerable quantity of silver is thus obtained which would otherwise be unavailable.

The operation is conducted in a series of hemispherical cast-iron pans, each capable of holding 6 or 8 tons of lead, and arranged in the manner represented by figs. 327

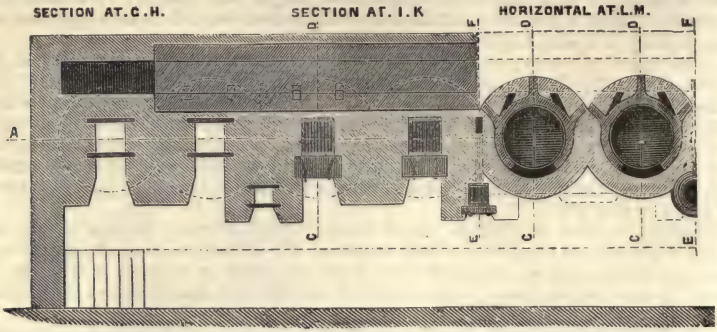


FIG. 327.

to 332. Beneath each of these pans is a fireplace, and between each pair of pans is a smaller-sized pan filled with melted lead for the purpose of warming the tool used for dipping out the lead crystals. A quantity of lead is melted in one of the pans at the centre of the series, and the dross collecting at the surface of the liquid metal skimmed off. The fire is then withdrawn, and while the melted lead is cooling it is stirred with an iron rod to promote crystallisation. As soon as a sufficient quantity of crystals have been formed, they are dipped out by means of a perforated iron ladle (fig. 329), and transferred to the pot on the right hand of the workman, care being taken to drain away from the crystals as much as possible of the liquid metal adhering to them. This operation is continued until three-fourths or more of the metal has been removed from the pan, and then the liquid portion is transferred to the adjoining pan on the left-hand side. In this way the metal is separated into two portions, one containing double or more than double the amount of silver originally in the lead, and the other considerably less. The precise extent to which the metal is allowed to crystallise and then removed from the liquid portion depends upon the amount of silver in the lead operated upon. With very poor lead a larger proportion is taken out of the pan in the form of crystals, and with lead containing much silver a smaller proportion is separated in the crystallised state. In the former case as much as seven-eighths of the metal is separated in the crystallised state, and this method of working is technically termed the low system; with lead richer in silver as little as two-thirds of the metal is dipped out in the crystallised state, and this is termed the high system; the whole of the lead under treatment being then kept in the pans, of which ten or fifteen are required. In the low system of working a smaller number of pans are used, and a considerable part of the crystals separated are laid aside and kept until there is a sufficient quantity for the full charge of the pots.

The same operation is carried out with the metal in the other pans right and left of the one in which the first portion of lead is crystallised; and by this mode of working, the metal finally transferred to the last pan to the right of the series, is almost free from silver, while that in the last pan to the left will contain as much as 0·7 to 1 per cent. of silver, or between 200 and 300 Troy ounces per ton. This appears to be about the extent to which the concentration of the silver can be carried with practical advantage by the application of Pattinson's process to argentiferous lead. In regard to this point C. Reich has shown that when the lead operated upon contains 1·442 per cent. of silver the crystallised portion contains 0·682 per cent. and the liquid portion 1·922 per cent., but when the silver in the lead operated upon amounts to 2·09 per cent. the crystallised portion contains 2·011 per cent. and the liquid portion contains 2·260 per cent. Moreover, the separation of the liquid metal from the crystals becomes more difficult as the amount of silver increases, and when it is as much as 2·3 per cent. there is a tendency to the solidification of the whole mass of metal at once.

The separation of silver from lead by Pattinson's method depends upon the circumstance that the melting point of an alloy consisting of lead with only a small proportion of silver is less than that of lead itself, and consequently this alloy remains liquid, while the lead solidifies in the form of granular crystals.

The extent to which silver can be thus extracted from lead does not in any case go beyond the limit of half an ounce per ton, and the lead operated upon in this way

should never retain more than that amount of silver; but, taking into account the cost of the operation and the loss of metal attending it, as well as the production of dross by oxidation, it is but rarely that lead with so small an amount of silver as 2 ounces per ton can be profitably worked in this way, so far as separation of the silver alone

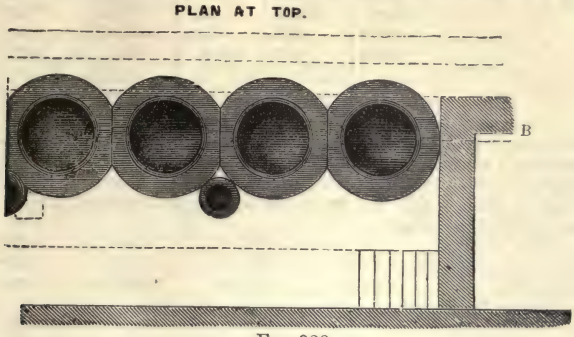


FIG. 328.

is concerned. When the silver amounts to 3 ounces per ton, its extraction by the Pattinson method is practicable, and consequently this method can be worked in many instances where the cupellation of lead would not be applicable. (See p. 435.) A further advantage of the Pattinson method is the purification of the lead by the oxidising action of the atmosphere upon the melted metal; at the same time the loss of lead is very much less than it is in cupellation.

The extent to which oxidation takes place during the treatment of lead by Pattinson's method varies according to the amount of silver and other metals in the lead; on the average, it is sufficient to produce a quantity of dross amounting to from one-fifth to one-third the weight of the lead operated upon. This dross is skimmed off and put aside for reduction in the same manner as litharge or the pot dross obtained in refining lead. The oxidation that takes place during the desilvering operation has the effect of purifying the metal.

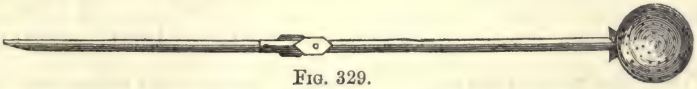


FIG. 329.

The arrangement of a series of ten pans is shown at different levels by the horizontal plan (figs. 327 and 328); fig. 330 represents a portion of the range of pans in vertical section longitudinally, showing the mode in which the pans are heated, by flues running round them, and figs. 331 and 332 show, in transverse sections, the flues leading from the sides of the pans into the main flue communicating with the chimney. The last pot on the right hand is called the market pot, since it is the final receptacle of the desilverized lead, which is ladled from it and cast into pigs. The pots on the left hand of this one are called working pots.



FIG. 330.

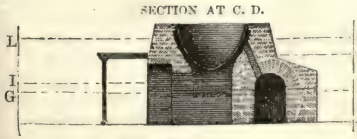


FIG. 331.

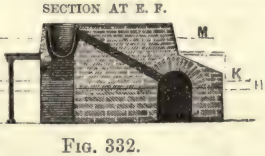


FIG. 332.

The following table of analyses by Streng of lead desilverised by this method will serve to show the proportions of other metals it contains:

	English	Stolberg	Billach	Eschweiler	Pirach	Altena
Lead	99·983	99·935	99·975	99·907	99·892	99·957
Antimony	0·015	0·007	0·012	0·053	0·061	0·021
Copper	trace	0·050	·007	0·026	0·041	0·016
Iron	0·008	·006	·006	0·003	·004	0·006
Zinc	0·004	·001	trace	0·011	·002	trace
	100·010	99·999	100·000	100·000	100·000	100·000

Besides the separation of some of the impurities in lead by the oxidation that takes place in working Pattinson's process, there is a concentration of some of these substances in the portion of metal remaining liquid. Baker has investigated this subject, and finds that copper is in this way separated from the lead crystallising out. In one case the original lead contained:

	Silver	Copper	Iron	Sulphur
1.	0·0046	0·0066	0·0065	trace
2.	0·0052	0·0154	0·0068	trace

The various products obtained in the operation contained:

		Silver	Copper	Iron
Rich pot:				
Before crystallising	—	0·0108	0·0344	0·0312
Crystals	25 parts	0·0052	0·0152	0·0086
Liquid portion	85 ,,	0·0140	0·0476	0·0122
Second pot:				
Before crystallising	—	0·0052	0·0154	0·0068
Crystals	95 ,,	0·0020	0·0066	0·0118
Liquid portion	25 ,,	0·0126	0·0286	0·0146
Third pot:				
Before crystallising	—	0·0020	0·0102	0·0118
Crystals	70 ,,	0·0010	0·0038	0·0198
Liquid portion	25 ,,	0·0100	0·0240	0·0082
Fourth pot:				
Refined lead	—	0·0014	0·0054	0·0112

From these results it was inferred that there is an alloy of lead with copper which has a low melting point, like the alloy of lead with a small proportion of silver that remains liquid in the Pattinson operation, and that in this way copper is separated from the lead as well as silver.

Nickel appears to be in like manner concentrated in the metal that remains liquid, and Baker found in operating upon lead containing from 0·0023 to 0·0057 per cent. of nickel, that this metal is not separated by oxidation, but that the liquid lead contains as much as 0·0043 and 0·0072 per cent.

In proportion as the amount of silver in the alloy increases, the difference between the melting point of the alloy and the melting point of lead decreases, and consequently the separate crystallisation of the lead is either prevented, or, when it does take place, there is much greater difficulty in draining away from the lead crystals the argentiferous alloy. Reich has investigated this subject, and the results arrived at by him are given in the following table:

Amount of Silver in the melted Lead before crystallising	Amount of Silver in the drained crystals	Amount of Silver in the residual liquid metal
Per cent.	Per cent.	Per cent.
0·704	0·390 to 0·466	1·025
0·732	0·318 ,, 0·374	1·076
0·966	0·410 ,, 0·680	1·450
0·988	0·390 ,, 0·624	1·530
1·442	0·682	1·922
2·090	2·011	2·260
2·116	1·728 ,, 2·216	2·248
2·206	2·212	2·264

The removal of the lead crystals, besides being a laborious operation, is one that causes considerable wear and tear of the pans, and several attempts have been made to economise labour by adapting machinery for this purpose and for the stirring of the lead while it is cooling. The apparatus represented by fig. 333 has been introduced with this object. It consists of a windlass and crane (*a b*) so placed that a

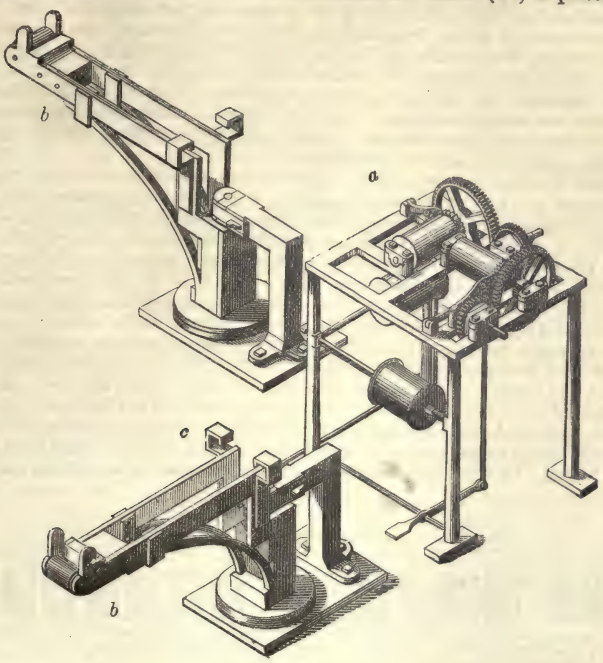


FIG. 333.

chain attached to the shank of the ladle is wound up on the windlass, and the ladle drawn up filled with crystals out of the pans. The workmen guide the handle of the ladle and place it under the catch (*c*) while the crystals are draining, and then by turning the crane the ladle is readily moved until it comes over the adjoining pan, into which the crystals are to be transferred. Worsley's apparatus for stirring the metal consists of a vertical shaft running in a step at the bottom of the pan and furnished with radiating arms. The lead was melted in a separate pan and then run into the crystallising vessel, and when the crystallisation had gone far enough the enriched liquid metal was drawn off into moulds through tapping holes at the sides of the crystallising vessel. This mode of working has not as yet proved successful.

When lead and zinc are melted and stirred together and then slowly cooled, the two metals separate almost completely; the zinc being specifically lighter than lead, it collects at the surface of the lead, and having a higher melting point it solidifies first. Mr. Parkes observed that by treating argentiferous lead in this way the silver was separated from the lead and retained by the zinc.

In operating upon lead by this method two cast-iron pans are used; one, capable of holding several tons of lead, for melting the lead, and the other one, of much smaller dimensions, for melting the zinc. The temperature of the melted lead is raised to the melting point of zinc, and then about a twentieth of its weight of melted zinc is ladled out of the small pot, mixed with the lead, the whole well stirred, and then allowed to cool gradually. When the zinc has solidified at the surface it is skimmed off with a perforated ladle, and the lead remaining in the liquid state contains about half an ounce of silver per ton.

The metal skimmed off retains some lead, and to separate this it is heated to a temperature above the melting point of lead, but not so high as the melting point of zinc, in a cast-iron retort set over a furnace and inclined so that the lead separating by liquation runs into a cast-iron pan placed at the end of the retort, and is set aside for further treatment with zinc. When the alloy of zinc and silver has been in this

way drained of lead, it is distilled with lime and charcoal in a retort so as to distil off the zinc from the silver, which is much less volatile. The chief difficulty encountered in working this process is in the separation of zinc from the desilverised lead. The use of superheated steam as an oxidising agent, introduced for this purpose by Cordurié in 1866, has been found effectual; and lead containing 0·75 per cent. of zinc has been purified in this way so as to retain only mere traces of zinc.

The extraction of silver from black copper by the method of liquation, which was formerly the only way of effecting the separation of these metals on a large scale, is now very rarely practised, and the method of amalgamation by which it was superseded has likewise been to a great extent discontinued in favour of methods of treatment which are more economical. In most instances the desilverising treatment is carried out with the copper regulus, consisting chiefly of cuprous sulphide, and containing the silver in the state of sulphide.

In order to extract silver as silver chloride from argentiferous copper regulus, it is first ground to a fine powder and roasted in a reverberatory furnace, until all the silver is converted into sulphate, and the other metals are in the state of oxides or insoluble basic sulphates. On treating a portion of the roasted material with water, it should yield an almost colourless solution that gives a precipitate of silver chloride on adding a few drops of hydrochloric acid. The mass is then removed from the furnace mixed with from 1 to 6 per cent. of sodium chloride, and again roasted at a temperature barely approaching redness, in order to avoid loss of silver by volatilisation as well as the melting of the chloride. If the copper regulus operated upon be free from lead, zinc, antimony and arsenic, and the first roasting has been properly conducted, the product of the second roasting will contain but little iron and copper in the state of chlorides, but the whole of the silver will be in that state. It is then lixiviated, while hot, with a concentrated solution of sodium chloride in tubs furnished with false bottoms covered with filters of linen cloth. These tubs (*a a*, fig. 334) are placed on a truck (*d*) mounted on wheels and running upon rails (*c c*) so that

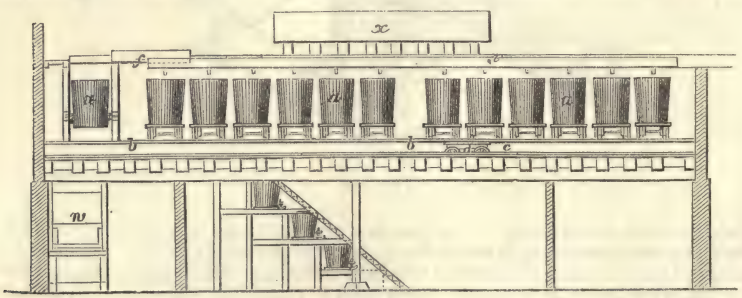


Fig. 334.

they can be transferred to a gallery (*b b*) underneath a trough (*e*) by which the sodium chloride solution is run in from a cistern (*x*). This solution is heated by steam, and in filtering through the roasted material in the tubs dissolves the silver chloride. After escaping from the lower end of the tubs it passes by the trough (*g*) into a tank (*h*, fig. 335) situated at such a level as to supply the tubs (*i i i i*) in which the silver is precipitated by copper. The liquid is then run off into the tubs (*l l l*) also containing finely divided copper; afterwards passing through two more rows of tubs (*m* and *n*), containing scrap iron to precipitate the copper, into the tank (*o*), which also contains some scrap iron, and it is then pumped up into the reservoir (*p*).

When the material in the tubs has been extracted, it is washed with water, and for this purpose the tubs are transferred to the tram road (*z*) beside the cisterns (*q r s*), the last of which contains clean water, while the others contain water that has been used once or more for washing the contents of the tubs. Each tub is first filled from the cistern (*q*) and the liquid allowed to run into the trough (*g*), then from the cistern (*r*), and the liquid run into the tank (*t*) is pumped up into the cistern (*q*), then from the cistern (*s*) and the liquid run into the tank (*u*) is pumped up into the cistern (*r*). The tubs are then carried forward and tipped over, so as to discharge their contents upon the table (*w*) through the opening (*t z*).

The extracted residue should not contain more than 0·03 per cent. of silver, and when the amount is greater it is again roasted and lixiviated, otherwise it is treated for the extraction of copper, as already described. The precipitated silver collecting in the tubs (*i* and *l*) is in the form of a fine crystalline powder. It is removed

every week and washed with dilute hydrochloric acid, then pressed, dried, and refined. The washing of the silver is carried on in the space (*y*).

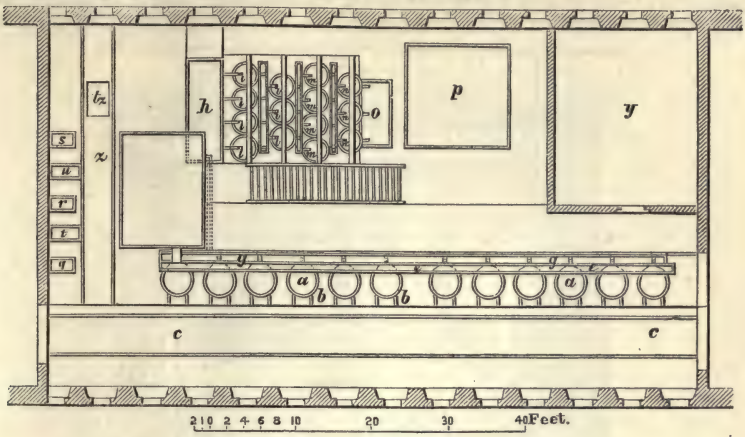


FIG. 335.

The precipitated copper in the tubs (*m n*) is again used for precipitating silver, and the liquid containing sodium sulphate which is transferred to the tank (*p*) is sometimes evaporated for the sake of obtaining that salt.

Black copper is sometimes treated by this method for the purpose of extracting the silver it contains; the metal, which should not contain more than about 10 per cent. of lead or antimony, is crushed to a fine powder and roasted with sodium chloride for several hours, with constant stirring meanwhile. During the latter stage of the roasting the heat is increased for the purpose of decomposing antimonial compounds. The roasted material is then finely powdered and lixiviated with sodium chloride solution in the manner already described.

The treatment of argentiferous speise is more difficult on account of the antimony and arsenic which this product often contains, and long continued roasting is requisite in preparing the material for lixiviation.

Sodium thiosulphate is sometimes used instead of sodium chloride for dissolving silver in the state of chloride, and this method of treatment has been found advantageous in working the rich silver ores, containing cobalt and nickel, which occur in the neighbourhood of Joachimsthal in Bohemia. The ores are coarsely powdered and roasted in reverberatory furnaces for several hours in contact with steam. The roasted material is then ground up with from 4 to 10 per cent. of sodium chloride, and if requisite some ferrous sulphate is mixed with it. After roasting this mixture again in contact with steam, the silver should be almost entirely extracted by solution of sodium thiosulphate. The mass is then sifted, moistened with water, and left for a time, in order that the silver may be more completely converted into chloride; it is then washed with hot water to remove salts of iron, cobalt, nickel, zinc, copper, and lead; a small quantity of silver is also extracted at the same time. The washed material is then mixed with a cold dilute solution of sodium thiosulphate which dissolves the silver chloride, and after separating this solution from the residue, the silver is precipitated as sulphide by adding a solution of sodium sulphide; the silver sulphide is collected, washed, and dried, and then melted with iron, to separate the silver in the metallic state.

The use of sodium thiosulphate as a solvent of silver chloride in the treatment of argentiferous copper regulus is more advantageous than that of sodium chloride, since it dissolves the silver chloride in much larger proportion; consequently the volume of liquid to be dealt with is relatively much smaller, and the operation requires less time.

In precipitating the silver as sulphide, by adding solution of sodium sulphate, the thiosulphate is left in solution, and can be used again in subsequent operations on fresh quantities of roasted regulus.

In both these methods the result of the first roasting of the copper regulus is to convert the silver into the state of sulphate, which is a salt sufficiently soluble to be extracted with water alone.

When the silver is extracted by dissolving it in the state of sulphate, the copper regulus is roasted in double reverberatory furnaces of the kind represented by

figs. 336 to 339. The lower hearth (*a*) is formed of fire brick bedded upon a layer of loam, and above the arch which forms the working chamber is the upper hearth (*o*), also covered with an arch and communicating with the lower hearth by the channel (*n*), which is closed by a lid at the upper end, as shown in figs. 337 and 338.

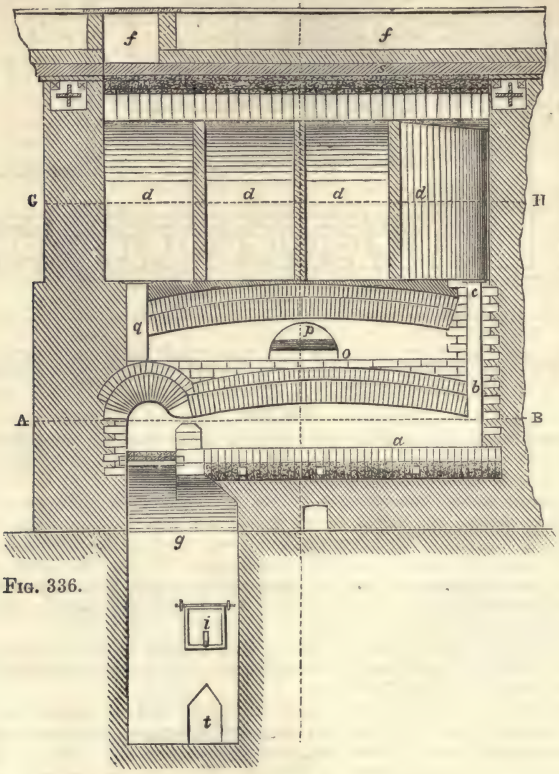


FIG. 336.

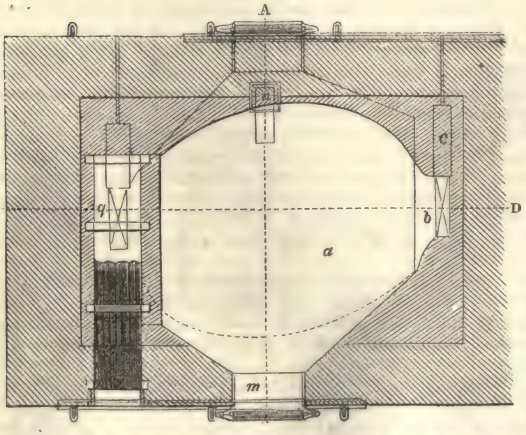


FIG. 337.

The lower working chamber also communicates by means of the flue (*b*) with the condensation chamber (*d d d*), and this flue is provided with a damper (*c*) by which it can be closed. The upper working chamber communicates with the condensing chamber by the flue (*q*). The working doors (*m* and *p*) of the lower

and upper hearths are provided with supports for tools. The ash pit (*g*) communicates by the opening (*x*) with the tunnel (*l*), running beneath several of these furnaces, and the opening (*x*) can be closed by a lid (*i*) worked by the rod (*h*) to regulate the admission of air beneath the fire-grate. The ashes are removed occasion-

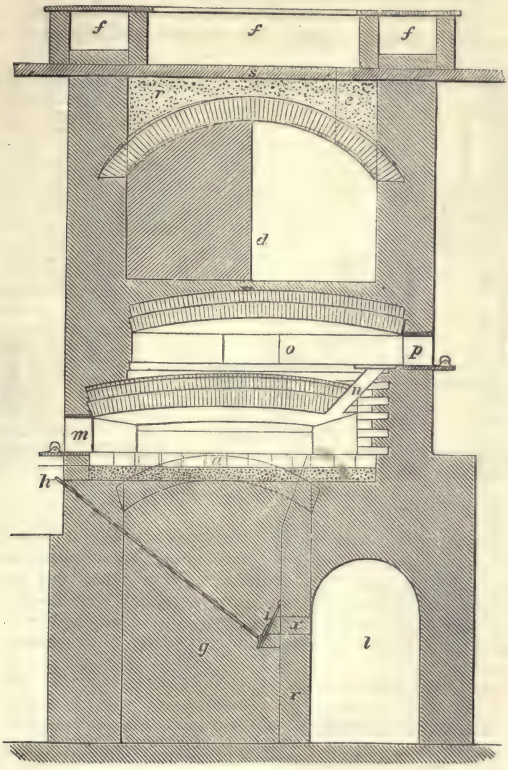


Fig. 338.

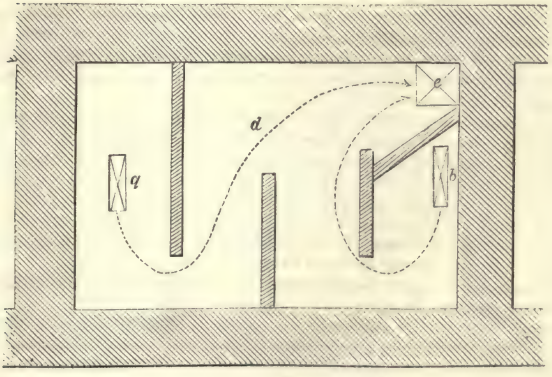


Fig. 339.

ally through the door (*t*). The condensation chamber (*d d d d*) communicates by the vertical flue (*e*, figs. 338 and 339) with the horizontal flues (*f f f*), which are covered with iron plates and serve for drying the desilverised material.

The roasted material when cold is lixiviated with water at a temperature of 70°

in tubs (A, fig. 340) fitted with false bottoms, several of them being placed in a row so that water or dilute sulphuric acid can be run into them from the leaden pipes (*b* and *a*). The solution of silver sulphate running out from the bottom of these tubs passes into a settling tank divided into two parts (B and C) by a vertical partition, then through a row of tubs corresponding to D, containing precipitated copper for the precipitation of the silver. The liquid discharged from these tubs does not contain much silver, but it is again brought into contact with sheets of copper in the

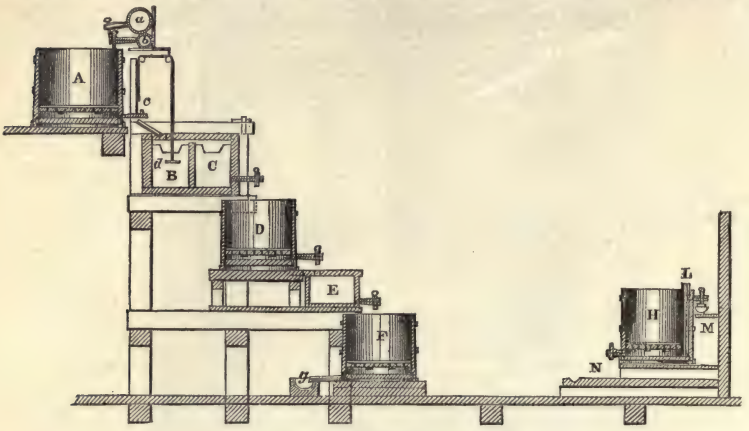


FIG. 340.

long tank (E), and in the tubs of the row corresponding to (F), from which it is run off through the trough (*g*) into a reservoir, and pumped up again for further use.

The copper regulus operated upon should contain about 80 per cent. of cuprous sulphide; it is ground very fine and then spread over the upper hearth of the furnace, which has been previously heated. When quite dry it is mixed with about 5 per cent. of coal, and well stirred for some time to prevent the formation of lumps of basic ferric sulphate.

A certain amount of ferrous sulphide is requisite to facilitate the formation of cupric sulphate, but when the material operated upon contains much more than 11 per cent. of ferrous sulphide, and but little cuprous sulphide, the silver cannot be so completely converted into sulphate. The presence of lead sulphide or antimonous sulphide in the regulus interferes with the formation of silver sulphate by causing the material to cake in roasting. Metallic zinc, antimony, or arsenic, also cause loss of silver, either by volatilisation in the roasting, or by the formation of silver antimonate and silver arsenate, which are not readily decomposed by sulphuric acid. For these reasons the extraction of silver as sulphate is not applicable to ores or other materials which do not contain copper combined with sulphur, or even to copper ores containing arsenic, antimony, zinc, or lead.

Silver is sometimes separated from copper regulus by means of hot dilute sulphuric acid. The regulus to be treated in this way should not contain much iron; it is roasted in the state of powder, and then mixed with the acid in wooden tubs into which steam is forced, to heat the liquid. The cupric oxide in the roasted material is thus dissolved as sulphate, while the silver is almost entirely left in the residue, together with ferric oxide, antimonates, and any gold that may be present. The solution of cupric sulphate is drawn off and crystallised, and the argentiferous residue is either melted with lead, or the silver is extracted in the wet way.

Argentiferous black copper is also treated in a similar manner with dilute sulphuric acid in order to separate the silver it contains.

The cuprous iron pyrites employed as a source of sulphur in the manufacture of sulphuric acid often contains a small proportion of silver, and in treating the burnt pyrites for the extraction of copper (p. 417) the silver it contains is now separated by a method introduced by Mr. Claudet. In roasting the burnt pyrites with sodium chloride the silver is converted into chloride, and sufficient sodium chloride remains undecomposed to dissolve the silver chloride when the roasted material is extracted with water. The liquor obtained by lixiviation, containing about three grains of silver in the gallon, is mixed with a sufficient quantity of a soluble iodide to convert the silver into iodide, and when left to settle a precipitate is deposited, consisting of silver

iodide, lead chloride, lead sulphate, and cuprous salts. The clear liquid is then run off, and the precipitate, after being washed with dilute hydrochloric acid to remove copper, is decomposed with metallic zinc. By this means zinc iodide is formed which can be used for treating fresh quantities of liquor, and the silver is separated in the metallic state, together with some lead, by the decomposition of lead chloride by the zinc.

Refining of Silver.--The silver obtained by cupellation of argentiferous lead generally retains a certain amount of impurity, for the separation of which it is sometimes subjected to further treatment in a reverberatory furnace with a fixed concave hearth formed of a layer of marl with a layer of clay and broken bricks beneath it. The charge consisting of about a ton of silver is placed on this hearth, covered with some coal dust or charcoal, and slowly melted down ; the melted metal is then stirred, the dross skimmed off, and some bone ash thrown upon the surface ; sometimes a blast of air is applied to facilitate the oxidation of the impurities, and when the silver has been kept in this state for several hours, it is ladled out into ingot moulds.

The precipitated silver obtained by the decomposition of silver sulphate (p. 444) is refined by melting it down in a furnace of this kind, and skimming off the slag and dross formed by the oxidation of the copper present in the precipitate, together with calcium sulphate and other substances.

Smaller furnaces which have moveable hearths formed of bone ash are also employed for refining silver, and the operation is carried out almost exactly in the same manner as the cupellation, but as the proportion of lead oxide formed is much smaller, it is chiefly absorbed by the porous material of which the test is constructed. The loss of silver by volatilisation is, however, sometimes considerable; and it is largest when a blast of air is used and the silver operated upon contains much antimony or other volatilisable metal.

The construction of the refining furnace with moveable hearth is represented by figs. 341 and 342. Except in dimensions this furnace closely resembles the cupellation furnace (p. 432). The test (*d*) consists of a thick layer of bone ash pressed into the iron frame which rests upon the iron bars (*e e*) and can be drawn out when the operation is completed. The flame from the furnace (*b*) passes over the surface of the test and escapes by the flue (*f*) into a chimney.

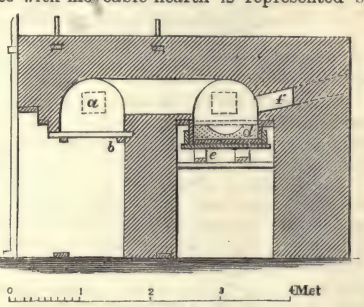


Fig. 341.

The quantity of metal operated upon at once varies from 1 to 5 hundredweight, and the operation lasts about six hours. By this treatment silver may be refined to such an extent as to contain only one tenth per cent. of impurity, or even less.

A still higher degree of purity may be attained by melting the metal in crucibles with nitre, or some oxidising flux.

It frequently happens that in the ores from which silver is obtained there is a minute proportion of gold which becomes concentrated in the silver, and is then worth separating. When this is the case, the refining of silver is carried out in the wet way, by treating it with sulphuric acid. This plan is also adopted for refining silver containing copper. The metal is first melted in large crucibles, heated to bright redness in furnaces fed with coke, the hot air from these furnaces being made to heat the bars of alloy that are afterwards to be melted. About 2 or 3 per cent. of nitre is thrown into the crucibles containing the fused metal, to remove any oxidisable metals by converting them into slag, which floats together with the melted nitre upon the surface of the melted silver, and is removed with a perforated cast-iron ladle.

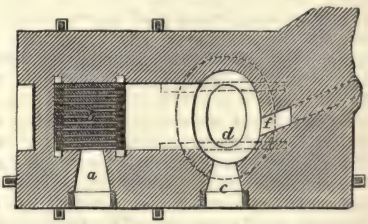


Fig. 342.

As soon as this skimming is over, the melted metal is granulated, by pouring it in a thin stream, from some height, into cold water, contained in an iron vessel. This granulated metal is placed in a hemispherical pan (fig. 343), about 3 feet in diameter, the sides of which are about 1 inch thick, and treated with sulphuric acid of specific gravity 1·84. A head (c), provided with a door (*p*), fits air-tight upon the flange

of the pan, and is connected with a bent leaden pipe (T T), passing through a trough (R) kept cool by a current of water flowing in by the funnel at the side, while the hot water is escaping through a tube in the upper part of the opposite side. The sulphurous oxide escaping from the pipe (T) is conducted into a lead chamber for conversion to sulphuric acid, or is otherwise disposed of.

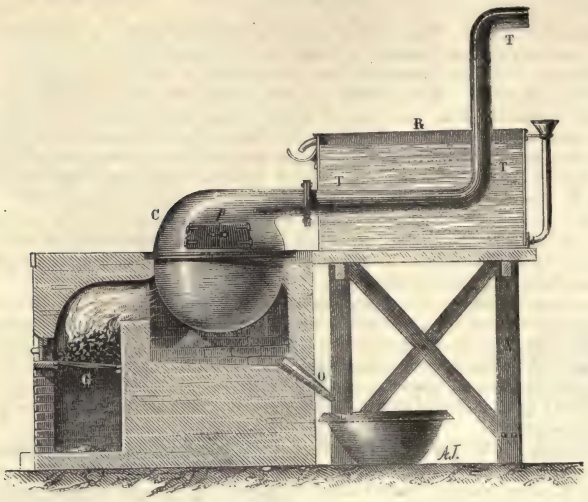


FIG. 343.

The pan is set in the furnace so that in case it should leak at any time the escaping liquid must flow into a hollow beneath and finally escape into a vessel placed under the tube (O). On this account the pan is heated from the side, the furnace (G) being separated from the hollow underneath the pan by a low wall.

By the action of the heated sulphuric acid, the granulated metal is dissolved, silver sulphate and cupric sulphate being formed, together with sulphurous oxide gas. Fresh quantities of sulphuric acid are added at intervals until all the metal is dissolved, the operation lasting about three hours.

When the alloy contains from 90 to 95 per cent. of silver, it dissolves entirely, yielding a clear liquid which is drawn off with a platinum siphon; but when the alloy contains less than 90 per cent. of silver, the solution remains turbid, and is then run into a leaden vessel, fitted with a cock about 2 inches above the bottom, mixed with nearly an equal volume of cupric sulphate solution, of spec. grav. 1·288 to 1·310, obtained from a previous operation, and steam is passed into the liquid through a leaden tube. By this means the suspended substance is almost entirely dissolved; the leaden vessel is then covered, and the liquid, after being kept hot for about two hours, during which it is allowed to settle, is drawn off by the cock into a thick leaden pan, where the silver is precipitated by adding copper turnings. The process is accelerated by frequent stirring, so as to detach the precipitated metallic silver from the surfaces of the pieces of copper. The reaction is complete when the dark blue solution ceases to yield a precipitate (silver chloride) with a solution of sodium chloride. When this point has been attained, the liquid is drawn off into another leaden pan, where any suspended portions of silver are allowed to settle. The vessel used for this purpose is generally that in which the turbid solution from the retorts is heated with solution of cupric sulphate. The clear blue liquid is finally evaporated and crystallised.

The precipitated silver is thoroughly washed, by placing it in a trough lined with lead and furnished with a fine sieve bottom. A leaden tube with a number of very fine perforations extends round the inner sides of the trough, and discharges a fine stream of warm water, which washes the silver, and then escapes through the sieve bottom. The water carries with it some particles of silver, which are allowed to settle in another trough below, and are afterwards collected and placed again in the washing trough. The water in the lower trough is let off at intervals through a cock placed at no great distance from the bottom. The silver precipitate is then removed, pressed, and melted.

Uses.—Silver has long been very generally employed for coining money, and for

this purpose it is alloyed with a small proportion of copper, which gives the requisite degree of hardness; the same alloy is also largely used for making articles for domestic use and for ornamental purposes. On account of the great power of silver to reflect light, it is used in making the reflectors used in lighthouses. Various articles of copper are coated with silver by uniting the two metals by heat, and rolling or hammering the mass into the required shape, so that when finished it presents a uniform layer of silver at the surface. The coating of articles with silver is now very largely effected by depositing the silver electrolytically, and in some instances the coating of silver is applied by rubbing the surface of the articles with an amalgam of silver and mercury, then driving off the mercury by heat and polishing.

The coating of glass with silver is effected by means of the reducing action of certain organic substances upon silver salts in the presence of ammonia, and this method has been applied not only to the silvering of mirrors for telescopes, but also to the making of large mirrors, and for various purposes of decoration. Liebig recommended the use of milk sugar with a solution of silver nitrate mixed with just enough ammonia to redissolve the precipitate first formed, and some caustic soda. The glass to be silvered is suspended so that the surface touches the liquid, and after some time it is coated with a deposit of silver.

Compounds.—Silver is monovalent in most of its compounds which are of importance industrially. The chloride, bromide, and iodide have the formulæ AgCl. AgBr. AgI.; the oxide Ag_2O corresponding to these compounds is a powerful base forming well-defined saline compounds with acid oxides, some of which are isomorphous with the corresponding salts of the alkali metals; and the sulphide Ag_2S is also a powerful basic substance which combines with acid sulphides forming a large number of sulphur salts, several of which occur naturally as minerals. The peroxide Ag_2O_2, corresponding in composition to the peroxides of hydrogen, potassium, etc., resembles these compounds in their general chemical relations. A compound of silver with nitrogen is formed when freshly precipitated silver oxide is treated with ammonia; it is easily decomposed when rubbed and explodes with great violence.

Silver unites with most other metals when melted with them, forming alloys which are sometimes nearly as white and ductile as silver, but are always harder than the pure metal; a very small proportion of copper has this effect of increasing the hardness of silver, and the presence of only a small amount of zinc, antimony, arsenic, bismuth, or tin, renders silver brittle, and liable to crack when rolled.

The alloys of silver and aluminum are harder than aluminum, and when the silver does not exceed 30 per cent. they are even more fusible than aluminum, and can be used for soldering this metal. The alloy containing 3 per cent. of silver is not acted upon by sulphuretted hydrogen; that containing 5 per cent. of silver has a fine white colour, takes a good polish, is tolerably malleable, and has about the same hardness as British standard silver. The alloy consisting of equal parts of aluminum and silver is brittle.

The alloys of silver with zinc are of a bluish-white colour. Döppler's reflector metal consists of silver with one-fourth its weight of zinc.

Silver mixes in all proportions with lead when the two metals are melted together; but when the melted mass is gradually cooled some separation takes place, and the interior contains a much larger proportion of silver than the outer parts.

Silver and copper may be melted together in any proportions; the alloys are almost as ductile as silver, they are much harder, more elastic, and take a higher polish than pure silver. When the silver amounts to more than 50 per cent., the colour of the alloy is white. The most important alloys of copper and silver are those used under the name of *standard silver* for coinage and for making utensils and ornaments. The alloy used for this purpose in the United Kingdom contains 7·5 per cent. of copper; its specific gravity is 10·20. In France three alloys are used, one containing 95 per cent. of silver for medals and plate, another containing 90 per cent. of silver for silver coin, and the third containing 80 per cent. of silver for jewelry work.

Silver solder is an alloy of silver with about half its weight of zinc and copper.

Alloys of silver and copper when solidified very gradually do not remain homogeneous throughout; but, according to the amount of silver they contain, the inner or outer portions of the mass contain a larger proportion of silver than the remainder. The alloy consisting of 71·9 per cent. silver and 28·1 copper does not separate in this way.

Although the alloys of silver with copper are white even when containing a large amount of copper, the colour is not so fine as that of pure silver, and in order to give articles made of such alloys an appearance more closely resembling pure silver, they are submitted to an operation termed *whitening*, by which the copper at the surface is oxidised and dissolved, leaving the silver almost pure.

SILVER OXIDE.

Formula Ag_2O. Molecular Weight 232.

Characters.—This substance is a dark brown powder sparingly soluble in water; its specific gravity is 7·14 to 7·25; it is readily decomposed by heat into metallic silver and oxygen, and when exposed to sunlight it is gradually decomposed; it is readily reduced by oxidisable substances, such as solution of sulphurous oxide, or by contact in the moist state with copper, zinc, or tin. Strong aqueous ammonia converts it into a fulminating compound which explodes with great violence when rubbed, especially in the dry state.

Preparation.—When a solution of a silver salt is mixed with caustic alkali out of contact with atmospheric air, silver oxide is precipitated, and after washing several times with boiled water it is dried at a moderate heat. The oxide may also be prepared by pouring a mixture of freshly-precipitated silver chloride and water into a boiling solution of caustic potash about 1·3 specific gravity. The chloride should be added very gradually, and the liquid kept boiling all the time.

SILVER CHLORIDE.

Formula AgCl. Molecular Weight 143·5.

History.—Silver chloride was certainly known to the older chemists in so far as it must have been a product of many of their operations, but the accounts given of this substance prior to 1595 are very vague; in that year Libavius clearly described the precipitate produced in solutions of silver by sodium chloride, and gave it the name of *lac argenti*. In 1608 Croll gave to the melted substance the name of *luna cornea*, and in the following century most of the characters of this substance became known.

Occurrence.—This substance occurs naturally as horn silver, accompanying ores of silver in various localities; it is most abundant in Peru, Chili, and Mexico; an earthy variety called buttermilk ore occurs at Andreasberg in the Hartz.

Characters.—Silver chloride as it occurs naturally is sometimes crystalline, forming octahedrons and cubes; its specific gravity is about 5·4, and it has a pearl grey or greenish colour, turns brown on exposure and is slightly translucent. The precipitated chloride is a white powder quite insoluble in water, but readily soluble in ammonia; it is also dissolved by solution of alkaline chlorides, forming double salts which are crystallisable, but are decomposed by water. Silver chloride is also dissolved by solutions of alkaline sulphites and thiosulphates.

At a temperature of about 260° silver chloride melts, forming a transparent yellow liquid, which on cooling solidifies to a horny translucent mass. At a high temperature it is slightly volatilisable, especially when mixed with other volatile substances. It is not decomposed when heated with charcoal, but is readily reduced by hydrogen at a high temperature, or when heated with alkaline carbonates. By contact with zinc, iron, or other easily oxidisable metals in the moist state it is soon reduced, especially if the water be acidulated with sulphuric acid, and the silver remains as a spongy mass. Weak alkaline solutions do not act upon silver chloride, but when boiled with a strong solution of caustic potash the chloride is converted into oxide. When boiled with solution of sodium carbonate and glucose, the chloride is decomposed and metallic silver separated.

By exposure to light silver chloride acquires a dark violet colour, the change being probably due to the formation of subchloride. Paper charged with silver chloride is very sensitive to light, and is used for taking photographs; the unaltered silver chloride being afterwards removed by means of a solution of sodium thiosulphate.

Preparation.—For the purposes of photography silver chloride is prepared upon the surface of the paper used for printing positives, by first saturating it with an alkaline chloride, and then floating the paper upon the surface of a solution of silver nitrate. The production of silver chloride is also an important point in the treatment of silver ores and other argentiferous materials for the extracting of silver; it is effected chiefly by the reaction which takes place between silver sulphate and alkaline chlorides, or the hydrochloric acid given off when mixtures of ferrous sulphate and sodium chloride are heated together, as in the roasting of copper regulus with sodium chloride. (See p. 440.)

SILVER SULPHIDE.

FORMULA Ag_2S. MOLECULAR WEIGHT 248.

Occurrence.—This substance occurs naturally as argyrose, or silver glance, and as acanthite; also in combination with other sulphides—with cuprous sulphide as stromeyerite AgCuS, with antimonous sulphide as miargyrite $Ag_2S.Sb_2S_3$, pyrargyrite $3Ag_2S.Sb_2S_3$, freibergite $4Ag_2S.Sb_2S_3$, stephanite $6Ag_2S.Sb_2S_3$, polybasite $9Ag_2S.Sb_2S_3$, with antimonous sulphide and lead sulphide as brongniardite PbS,Ag_2S,Sb_2S_3, and freieslebenite $2Ag_2S,3PbS,2Sb_2S_3$, with arsenous sulphide as proustite $3Ag_2S.As_2S_3$, and xanthoconite; with ferrous and ferric sulphides, as sternbergite ($Ag_2S.2FeS$). $3Fe_2S_3$. Silver sulphide also occurs, very frequently, associated with the sulphides of lead, copper, and zinc in varying proportions, as argentiferous galena, fahl-ore, and blende, and in some kinds of iron pyrites.

Characters.—Silver sulphide in the crystalline state generally presents forms of the regular system; the crystals are irregularly developed in dendritic and filiform masses; it has a dark grey colour and metallic lustre. The density is from 7·196 to 7·365. The artificially prepared sulphide has a density of 6·85.

Silver sulphide is not decomposed when heated out of contact with air, and it is but slowly oxidised when heated in the air, sulphurous oxide being given off while metallic silver remains; part of the sulphide is converted into silver sulphate, which requires a very high temperature for its decomposition, yielding then sulphurous oxide, oxygen, and metallic silver. The sulphide is decomposed by ignition in hydrogen gas, and the melted sulphide is decomposed by iron, but in the presence of cuprous sulphide or lead sulphide some of the silver sulphide remains unaltered. Both lead and copper decompose only part of the sulphide. Silver sulphide rubbed with mercury yields mercuric sulphide and silver, the latter forming an amalgam with the excess of mercury; chlorine gas acts upon the sulphide only when heated, and then slowly, but converts the silver entirely into chloride. When the sulphide is heated with sodium chloride it is but slightly acted upon and mere traces of silver chloride formed. When the sulphide is heated in contact with water vapour to a temperature insufficient for fusion, it is decomposed, and the reduced metal presents the same filiform appearance as the silver occurring naturally.

Silver sulphide is but little acted upon when digested with solution of ferric chloride or cupric chloride, but in the presence of sodium chloride it is partly converted into silver chloride, and sulphur is separated, while the solution contains a compound of cuprous chloride with sodium chloride. The formation of silver chloride takes place more readily when silver sulphide is digested with a solution of cuprous chloride in sodium chloride. It is possible that in the amalgamation of silver ores by the Mexican method, cuprous chloride may be formed by the action of metallic silver in the ore upon the cupric chloride used in the operation, or this effect may be in part produced also by the action of the mercury upon the cupric chloride, mercurous chloride being formed at the same time.

When silver sulphide is heated with a solution of cupric oxychloride, the sulphur is oxidised to sulphuric acid, the silver being separated in the metallic state, and cuprous chloride formed.

When silver sulphide is heated together with a considerable proportion of cupric sulphate to a temperature sufficiently high to decompose the cupric salt, the silver sulphide is converted into sulphate, and one of the methods of extracting silver from argentiferous copper regulus is based upon this fact.

SILVER SULPHATE.

FORMULA Ag_2SO_4. MOLECULAR WEIGHT 312.

Characters.—Silver sulphate is a colourless salt soluble in about 200 parts of cold water and 88 parts of boiling water. It separates as a white pulverulent precipitate on adding sodium sulphate to a solution of silver nitrate, but is crystallisable in anhydrous needles belonging to the trimetric system, and isomorphous with anhydrous sodium sulphate. When exposed to light it gradually turns green. The salt melts at a moderate heat, and at a high temperature is decomposed, leaving metallic silver; but it requires a higher temperature for decomposition than either cupric sulphate or ferrous sulphate, a circumstance which is of importance in the roasting of argentiferous copper regulus, since it admits of the ferrous sulphate and

cupric sulphate formed in the first stage of that operation being converted into basic ferric sulphate and cupric oxide, while the silver sulphate remains unaltered and capable of being extracted from the roasted material by lixiviation with water, and thus separated from the preponderating mass of insoluble copper and iron compounds with which it is associated. (See p. 444.)

Preparation.—It is chiefly in the extraction of silver from copper regulus that the production of silver sulphate is carried out, and then this salt is formed partly by the oxidation of the sulphide by atmospheric air, but chiefly by the action of sulphuric acid vapour upon the ulphide. (See p. 442.)

SILVER NITRATE.

FORMULA $AgNO_3$. MOLECULAR WEIGHT 170.

Characters.—This salt forms colourless anhydrous crystals belonging to the trimetric system; it dissolves in its own weight of cold water, and in half its weight of hot water; it is also soluble in four parts of boiling alcohol. The salt melts at 219°, and when cast into small sticks is used as a caustic in surgery under the name of lunar caustic. When applied to the flesh of animals it instantly destroys the vitality of the part touched. It is decomposed by exposure to light. In contact with organic substances the silver is reduced either to the metallic state or to oxide. On this account it is employed in the preparation of hair dye, and of ink for marking linen, etc.

Preparation.—Silver nitrate is easily prepared by dissolving the metal in nitric acid, and evaporating the solution until sufficiently concentrated to deposit crystals on cooling.

MERCURY.

Symbol Hg. Atomic Weight 200.

History.—The knowledge of this metal does not appear to have dated back so far as that of gold, silver, copper, iron, etc.; and the first mention of it is found in the works of Theophrastus about 300 B.C., where liquid silver *χυτὸν ἄργυρον* is spoken of as being obtainable by rubbing cinnabar and vinegar together in a copper vessel with a copper pestle. Discorides described this metal under the name of *ὑδράργυρος*, from *ὕδωρ* water and *ἄργυρος* silver, and gives the method of preparing it by distillation. The metal occurring naturally was described by Pliny as *argentum vivum*, and that obtained by cinnabar as *hydrargyrum*. Mercury was considered by the alchemists a constituent of all metals, and it was not until the time of Lavoisier that it was classed among the elementary substances.

Occurrence.—Mercury occurs naturally in the metallic state to some extent, but more frequently in combination, with either gold or silver, as amalgams, which are sometimes crystallised. It also occurs combined with chlorine, as horn quicksilver, Hg_2Cl_2, and more rarely as selenide and iodide. It occurs most abundantly in combination with sulphur as cinnabar HgS, which is the source from which mercury is chiefly obtained.

Some kinds of fahl-ore contain mercury in the state of sulphide. Ores of this kind occur in various parts of Hungary, and have the composition given in the following table:

Copper	36·39	34·23	30·58	32·80	39·40
Iron	7·11	9·46	1·46	5·85	7·38
Mercury	3·07	3·57	16·69	5·57	0·52
Silver	0·11	0·10	0·09	0·07	0·12
Antimony	26·70	33·33	25·48	30·18	31·56
Arsenic	trace	trace	trace	trace	trace
Sulphur	25·90	19·38	24·37	24·89	22·00

The chief localities in which mercury ores occur are Spain, Carniola in Southern Austria, California, Mexico, Peru, China and Japan. They are also met with on a smaller scale in France, Tuscany, and some parts of Germany.

Characters.—Mercury at the ordinary temperature is a very mobile but coherent liquid, of a bluish-white colour and metallic lustre. At a very low temperature it solidifies as a soft ductile mass. Its density in the liquid state is 13·559; it boils at 360°, and is converted into a colourless vapour, the density of which is 6·97 as compared with that of atmospheric air, and 100 as compared with hydrogen.

Mercury is not readily oxidised when exposed to atmospheric air at the ordinary temperature, unless it is in contact with greasy substances, but when heated in contact with atmospheric air it is gradually oxidised and converted into mercuric oxide. It combines readily with chlorine or bromine, and with sulphur or iodine, when rubbed with those substances; it also unites with many of the metals at the ordinary temperature. It is not acted upon by hydrochloric acid even when heated with it, but sulphuretted hydrogen or hydriodic acid is slowly decomposed when in contact with mercury. Strong sulphuric acid has no action upon mercury, unless heated together with it, and then, if the acid be in excess, mercuric sulphate is formed, and sulphurous oxide given off; but if mercury be in excess, mercurous sulphate is formed. Nitric acid dissolves mercury rapidly at the ordinary temperature, with evolution of nitrous fumes, forming mercuric nitrate if the acid is in excess, and when nitric acid is warmed with excess of mercury, basic mercurous nitrate is formed; dilute nitric acid dissolves mercury slowly, forming neutral mercurous nitrate.

Preparation.—The ores from which mercury is principally extracted contain the metal in the state of mercuric sulphide, associated with various argillaceous and earthy substances. The mercury is separated either by heating the ore in contact with atmospheric air, so as to oxidise the sulphur and form sulphurous oxide while the mercury is volatilised,—

$$\underset{232}{HgS} + \underset{32}{2O} = \underset{64}{SO_2} + \underset{200}{Hg}$$

or by heating a mixture of the ore with lime or some other substance capable of combining with the sulphur and separating the mercury in the metallic state. With lime the reaction which takes place is as follows:—

$$\underset{928}{4HgS} + 4CaO = 3CaS + CaSO_4 + \underset{800}{4Hg}$$

In both cases the mercury is volatilised and the vapour condensed by passing the gaseous products through a series of clay tubes or large chambers built of brick.

The mercurial fahl-ores which occur in Hungary are worked in a very rude way by roasting them in heaps surrounded by walls in which flues are formed, and the mercury is obtained as a by-product, much in the same manner that sulphur is obtained in roasting copper ores (see p. 401); in fact, the roasting of these ores is carried out mainly as a necessary preparation for smelting them as copper ores in the usual way. Part of the mercury is condensed in the upper layer of finely divided ore with which the heaps are covered, and when the operation of roasting is ended this is carefully removed and washed with water so as to separate the metallic mercury distributed amongst it.

The apparatus used for heating the ore sometimes consists of a number of close iron vessels, like retorts, heated in a galley furnace; reverberatory furnaces or kilns are also used in some cases.

The treatment of mercury ores in closed vessels admits of a more ready and complete condensation of metal than is the case when atmospheric air is mixed with the vapour, but it is more costly.

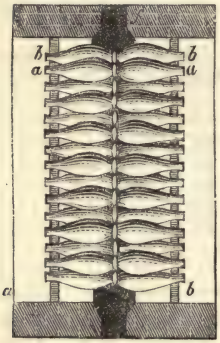


Fig. 344.

In Germany, sandstone containing a very small amount of cinnabar, varying from ·005 to ·01 per cent., is worked by distilling it in cast-iron vessels of the form shown in the accompanying drawing. The ore is broken into small fragments and about fifty or sixty pounds placed in each of the vessels together with some quick-lime. A number of these vessels are then arranged in rows in a galley furnace of the kind represented in plan, section and elevation by figs. 344, 345, and 346. The necks of the iron vessels (*a a* and *b b*) project beyond the side walls of the furnace, so that stoneware receivers containing some water can be adapted to them for the condensation of the mercury vapour. The iron vessels are then gradually heated to redness by making a fire upon the grate (*c*) extending from end to end, with an ash pit (*d*) beneath. In the arch covering the iron vessels openings (*e e*) are made by which the draught of the furnace is regulated.

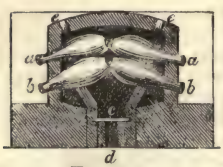


Fig. 345.

When the distillation is completed, the contents of the receivers are poured into a wooden bowl, where the metallic mercury sinks to the bottom, and the black substance suspended in the water is washed into a vat placed underneath. This black substance, containing mercury in the state of sulphide and oxide, is allowed to deposit, then dried and distilled with lime in the same manner as the ore.

A similar method of working mercury ore is practised in Transylvania, but stoneware retorts are used for the heating of the ores, and the operation is conducted in a very crude manner.

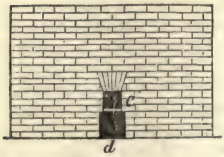


Fig. 346.

An improved form of apparatus for heating mercury ores is represented in vertical section lengthways by fig. 347. It consists of a series of cast-iron retorts (*a*) open at one end and each fitted with a lid by which the retorts can be completely closed and their contents kept from contact with atmospheric air. At the opposite end of each retort is a delivery tube (*b*) through which the mercury vapour escapes when the mixture of ore and lime in the retort is

heated. The delivery tubes (*b*) are connected with a tubular vessel (*c*) containing water and arranged much in the same manner as the hydraulic main used in gas works, the ends of the delivery tubes dipping just below the surface of the water. The retort is heated by the fireplace (I), and as the delivery tube dips under water a fresh charge of ore and lime can be introduced immediately after the contents have been worked off and drawn out.

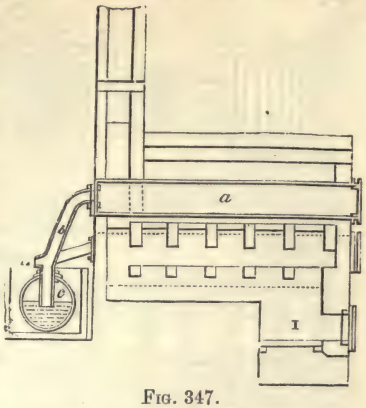


Fig. 347.

These retorts are arranged in sets of three within an arch placed over each furnace, as shown in the transverse section fig. 348, where three of these sets of retorts are placed side by side, and fig. 349 represents an elevation of the ends of the retorts to which the delivery tubes are attached, together with a longitudinal section of the cylindrical tube (c c) into which the ends of the delivery tubes (*b b b*) of the retorts are fitted. At one end of the hydraulic main there is a water valve (*g*) which serves to counteract the effects of unequal pressures caused by sudden expansion or contraction in the hydraulic main. The

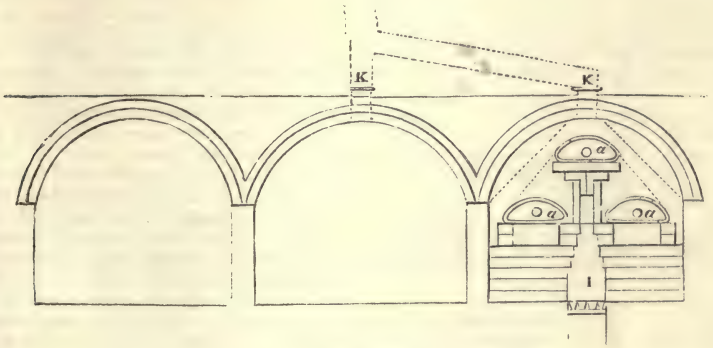


Fig. 348.

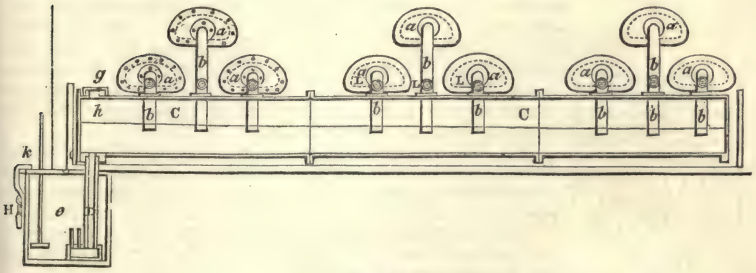


Fig. 349.

hydraulic main condenser is placed in a square trough made of wood, as shown in the section fig. 347, and water is made to flow through it by which the contents of the condenser are cooled. The condensed mercury collects at the bottom of the hydraulic main, which has a slight inclination, and the mercury flows towards the lower end (*h*) and falls through the tube (D) into the iron receiver (*e*), which is secured by a padlock (H) and is furnished with a graduated iron gauge rod (*k*), by which the quantity of mercury collected in the reservoir may be ascertained.

One of the forms of apparatus employed in Idria for the extraction of mercury

from its ores is represented by figs. 350 to 353. It consists of a kiln in which the mercury ore is heated in contact with atmospheric air and connected on each side with a series of chambers where the mercury vapour is condensed as it passes through them. Fig. 350 gives a general view of the apparatus in vertical section. In the furnace (*b*) fuel is burnt to heat the ore and the fire is regulated by the door (*a*). Above the fireplace are several arches indicated by the numbers 1 to 7, upon which the ore is placed through the opening (*d*) at the upper part of the kiln. The products of combustion, mixed with mercury vapour,

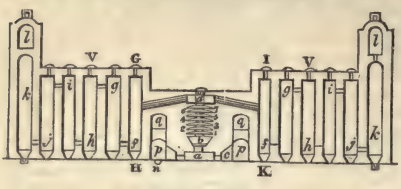


Fig. 350.

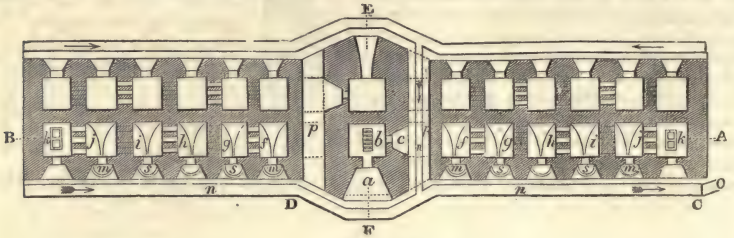


Fig. 351.

pass out of the kiln through the brick flues (*e e*) on each side, into the condensing chambers (*f g h i j k*) which are shown on a larger scale in the horizontal plan, fig. 351. It will be seen that the condensing chambers communicate with each other by openings placed alternately at the upper and lower parts of the chambers, so that the smoke and vapour pass up and down through the chambers until the chimney (*l l*) on each side is reached. During the passage of the gas and vapour, condensation takes place and the mercury collecting at the bottom of the successive chambers flows out into the basins (*m m*) placed opposite the doors of the condensing chambers which are shown in figs. 351 and 352. The condensed mercury collecting in these basins flows then into the trough (*n n*) and runs into a common reservoir in the direction of the arrows. The arched passages (*p p*) shown in figs. 350, 351, and 352, admit of access to the sides of the furnace and the arches (*q q*) figs. 350, 352 communicate with the flues (*e e*). The elevation of one half of the apparatus fig. 352 shows the position of the doors (*s s t t*) by which access can be gained to the condensing chambers (*f k*), fig. 350, and the doors (*u u*) of the kiln in which the mercury ore is heated.



Fig. 352.

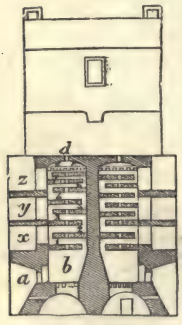


Fig. 353.

Fig. 353 represents the floors (*x y z*) corresponding to the doors (*u u*) of the kiln, and these floors are reached by stairs in different parts of the building. This section also shows the position of the fireplace (*b*) and of the arches (1 to 7) above it; (*d*) is the opening at the top of the kiln, and just below it are the brick flues (*e e*) by which the smoke and vapour escape into the condensing chambers.

In charging these kilns large blocks of the ore which is poorest in mercury are placed upon the lower arches above the fireplace, above this the smaller fragments of ore are placed, and on the middle arches the small ore containing a larger amount of metal is placed in small pots. Upon the upper arches the more finely divided portion of the ore is placed also in pots. All the doors are then closed and the fire being lighted, it is kept up until the whole furnace has acquired a cherry red heat. The distillation lasts from ten to twelve hours, and the kiln is then allowed to cool during several days, after which the exhausted residues are drawn and a fresh charge put in.

At Almaden in Spain the mercury ore is heated in contact with atmospheric air in

brick kilns, and the mercury vapour is condensed in earthen pipes called aludels, a number of which are fitted together so as to form long channels for the products of combustion to pass through. The general arrangement of this apparatus is represented by figs. 354 and 355. The kiln (*d*) in which the ore is placed is separated from the fireplace (*b*) by a perforated brick arch on which the mercury ore rests. The fuel is introduced through the arch (*a*) and below the fireplace is the ash pit (*c*). In fig. 355 the same parts are shown in plan. At the top of the kiln (*d*) there are at one side a number of openings (*f*) which communicate with the rows of aludels placed on the sloping terrace, at the lowest point of which there is a gutter (*g*) into which the condensed mercury runs out of a hole in the last aludel, and then passes through the wooden pipes (*h h*) into cisterns filled with water.

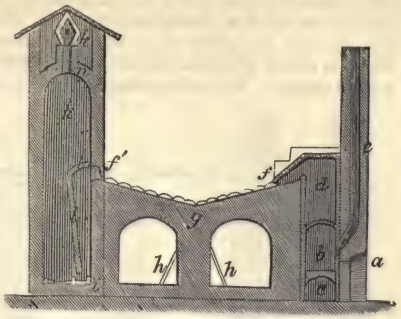


Fig. 354.



Fig. 355.

The uncondensed mercury vapour passes on into the aludels on the opposite sloping terrace and then through an opening (*f'*) into a chamber (*k*), where it is made to pass to the bottom by the partition (*l*), and is then condensed and deposited in the cistern (*i*). At the top of this chamber is an arch (*n*) with an opening through which the uncondensable gas escapes into another small chamber (*k'*).

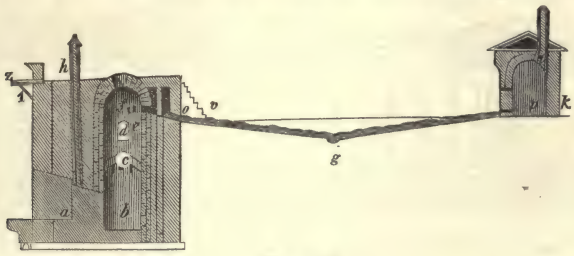


Fig. 356

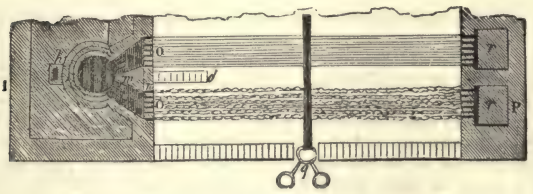


Fig. 357.

The arrangement of the series of aludels is shown more distinctly by figs. 356 and 357, as well as the connection between them on one side with the kiln and on the other with the condensing tower (*k*).

The loss of mercury in working ores in this kiln is very considerable, since the aludels are readily broken and the connections cannot be kept perfectly tight. In addition to this disadvantage, the escape of mercury vapour has a prejudicial effect upon the workmen, and as the operation has to be stopped when each charge of ore has been exhausted, much time is lost in this way while the kiln cools sufficiently to be opened for removing the residues.

The furnaces constructed by Hähner in Idria are intended to admit of continuous

working. They are represented by figs. 358 and 359. The mercury ore is heated in the shaft (*a*) by means of a fire made on the grate (*c*); this shaft is closed at the top and the ore is fed in through a hopper (*b*). In the flue (*f*) which connects the shaft with the first of a series of condensation chambers (*g g g*) there is a sliding damper (*e*), which is closed while the exhausted ore is being drawn from the shaft and replaced by a fresh charge. The condensing chambers (*g g g*) are constructed of brick, and are

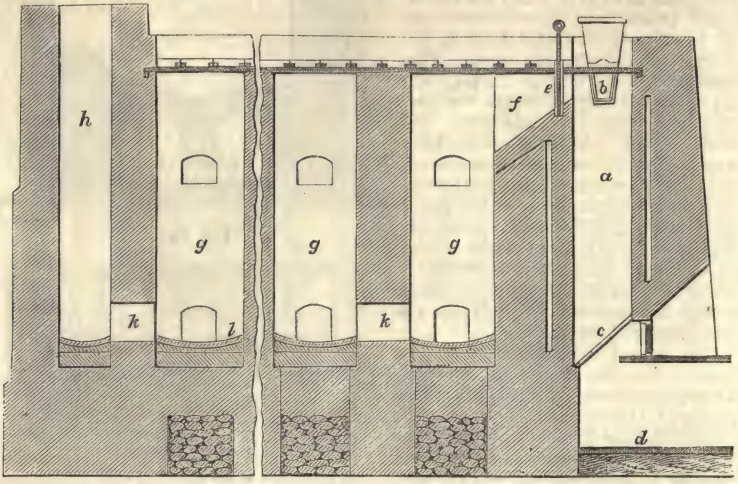


Fig. 358.

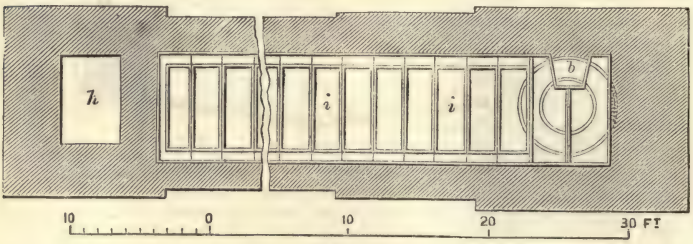


Fig 359.

covered on the top with iron plates (*i i*, fig. 359), over which a stream of cold water is made to run. These chambers are six in number, communicating by the openings (*k*) at the bottom, and the last of the series communicates in the same way with the chimney (*h*). The floor or sole (*l*) of each condensing chamber is made of loam beaten down upon a bed of brick, to form a hollow in which the condensed mercury collects.

In charging this kiln some bricks are placed upon the sloping grate (*c*) and upon them a quantity of brushwood or coal; alternate layers of ore and coal are then thrown in until the shaft is filled to the requisite height, and after setting light to the brushwood the fire is made to burn gradually for several hours. After the end of the second day the fire should become visible at the top of the materials in the shaft, and then the regular charging of fresh ore and fuel is commenced, about seven hundredweight of ore, together with 3 or 4 per cent. of fuel, being thrown in through the hopper (*b*) at intervals of an hour or rather less, while, at the same time, the exhausted residue of the ore is drawn out from the bottom of the shaft into waggons running upon a tramway under the kiln.

Even in the kilns constructed on this plan there is a great waste of mercury, amounting to about one-third of the contents of the ore; but these kilns do away with the necessity for interrupting the operation, and they are, in this respect, an improvement upon those previously described. In some places the soles of the condensation chambers are constructed of cast iron, with a tube through which the mercury collecting upon them runs out into a receiver outside.

Reverberatory furnaces are also used for extracting mercury from its ores. Those employed in Idria are represented together with the condensing arrangements by figs. 360 to 362.

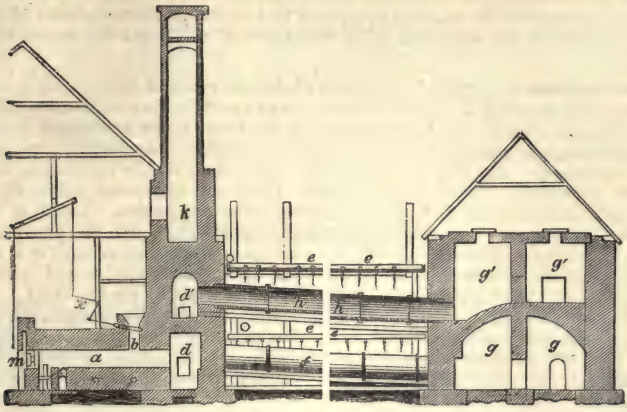


Fig. 360.

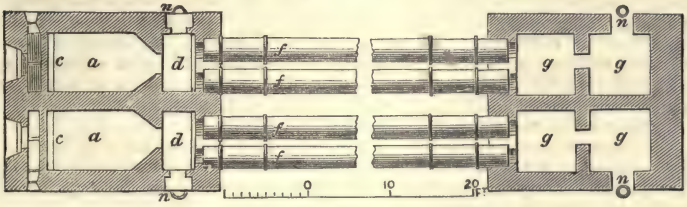


Fig. 361.

The furnace (*a*) is fed through the hopper (*b*) and closed by the sliding door (*m*). Between the hearth and the fire bridge is a space (*c*) for receiving the roasted ore. The mercury vapour passes from the furnace first into the chambers (*d d*), and then through long cast-iron pipes (*f f f f f*) kept cool by water dropping on them from the gutter (*e e*). The uncondensed vapour escaping from these pipes passes into the two chambers (*g g*), from thence into other two chambers (*g' g'*) above, and then into another set of cast-iron pipes (*h h*) also kept cool by water supplied from the gutters (*e e*), and lastly the uncondensable gas escapes through the brick chamber (*d'*) into the chimney (*k*), which is divided into compartments as shown in the transverse section fig. 362, by two vertical walls (*i i*) that make the gas pass up and down before escaping into the air through the openings (*l l*) at the top of the chimney.

In working this furnace the ore is spread upon the hearths (*a a*), the working doors (*m*) closed securely, and the ends of the hearths nearest to the door are heated to redness; the fire is then let nearly out, the ore stirred for a few minutes, then heated again to redness, and lastly raked down through the opening (*c*). The hot ore on the middle of the hearth is then drawn forward, and that at the further end of the hearth placed in the middle, while a fresh charge of ore is introduced through the hopper (*b*), and then the heating of the ore to redness is carried out again as before. In this way the fresh ore is gradually heated while a part of the charge is being roasted. The mercury collects chiefly in the lower tubes (*f f*) and the chambers (*g g*) and part of it runs out from them into the vessels (*n n*). The deposit in the chambers (*g' g' d' d'*) and that in the iron tubes contains about fifty per cent. of mercury; it is first dried, and after the mercury has been drained off the residue is distilled.

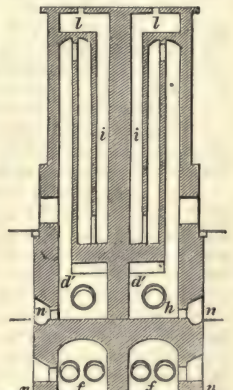


Fig. 362.

Uses.—Mercury is employed for a great number of purposes. On account of its great density and uniform expansion it is used in the construction of thermometers, barometers, and other kinds of experimental apparatus. A considerable quantity is used in the extraction of silver and gold from their ores; it is also used in various forms of combination for medicinal purposes, and several of the compounds of mercury with other metals are employed under the name of amalgams for various technical purposes.

Compounds.—Mercury forms two well-defined series of compounds, mercuric compounds, in which it is divalent, and mercurous compounds, in which it is apparently monovalent. The compounds of the latter series correspond in constitution to the cuprous compounds, and are readily converted into mercuric compounds by oxidising agents; but they are generally much more stable substances than the cuprous compounds. Both mercuric oxide HgO, and mercurous oxide Hg_2O, are basic, and combine with acid oxides, forming saline compounds. There is but one compound of mercury with sulphur, mercuric sulphide HgS, and the precipitate obtained on adding sulphuretted hydrogen to solutions of mercurous salts is a mixture of this sulphide with metallic mercury. The chlorides, bromides, and iodides are represented by the formulæ $HgCl_2$, $HgBr_2$, HgI_2, and Hg_2Cl_2, Hg_2Br_2, Hg_2I_2.

Many of the mercuric compounds combine with corresponding compounds, forming a great number of double salts, in which the mercury compounds act the part of acid; thus, for instance, mercuric oxide combines with potassium iodide, forming potassio-mercuric iodide KI, HgI_2, or, as it is sometimes called, potassium iodo-hydrargyrate.

Mercurial compounds of both series combine with ammonia, forming a great variety of substances, in which the mercury takes the place of part of the hydrogen in ammonium. The substance known as white precipitate is of this nature, and its composition is represented by the formula $(NH_2Hg)Cl$. Hahnemann's soluble mercury is another compound of this kind, the constitution of which is represented by the formula $(Hg_3HN)NO_3H_2O$, corresponding to ammonium nitrate, in which three-fourths of the hydrogen of the ammonium is replaced by mercury.

Mercury also forms compounds with alcohol radicles.

The alloys of mercury with other metals are called amalgams, and those of definite composition are solid, while the liquid amalgams are probably solutions of those substances in mercury; in many cases the excess of mercury can be separated from the solid amalgam by pressure.

Mercury unites with the alkali metals with very considerable evolution of heat; the alloy of potassium with 70 parts of mercury is solid; that with 30 parts of mercury is hard and brittle. The alloy of sodium with 30 parts of mercury is hard and crystalline; that with 60 parts of mercury becomes pasty when slightly warmed.

The amalgams of barium, calcium, etc., are analogous to those of the alkali metals, and they may be obtained by decomposing saturated solutions of the respective salts by means of sodium amalgam.

Aluminum, according to Deville, does not unite with mercury to form an amalgam.

Magnesium forms with mercury a solid amalgam when the metals are heated together. Zinc unites with mercury slowly at the ordinary temperature, but readily with the aid of heat. The alloy of zinc with one-eighth its weight of mercury is very brittle; that with one-sixth of mercury melts at the boiling point of olive oil. The alloy containing 80 per cent. of mercury is brittle and pulverulent; it is used for coating the rubbers of electrical machines.

When sheet zinc moistened with a dilute acid is rubbed with mercury, hydrogen is disengaged and the surface of the zinc is amalgamated; the zinc plates of galvanic batteries are prepared in this way.

Lead unites readily with mercury, forming an amalgam which is liquid even when containing one-third its weight of lead. The metals contract considerably in uniting and the amalgam has a higher specific gravity than either of them. The presence of a very small proportion of lead—about 0·02 per cent.—in mercury renders this metal more suitable for barometers and thermometers, since it is then less disposed to form globules that adhere to the glass.

Copper does not unite very readily with mercury except in the presence of an acid or when one or other of the metals are in the state of a salt, as when mercury is rubbed together with verdigris, or copper foil is immersed in a solution of a mercury salt. When mercury is covered with a solution of cupric sulphate and placed in contact with the negative pole of a voltaic battery while the positive pole is connected with a wire dipping into the cupric sulphate solution, it becomes saturated with copper.

The alloy of copper and mercury containing about 30 per cent. of copper is crystalline and harder than zinc; it has the property of becoming soft and plastic when rubbed in a warm mortar, and then of becoming hard again when kept; on this account

it is sometimes used by dentists for stopping decayed teeth. This alloy is prepared by mixing mercurous sulphate and finely divided metallic copper under warm water. After rubbing them together for several minutes the water is poured off and replaced by fresh, this being continued so long as the water has any blue colour.

Silver unites with mercury but slowly at the ordinary temperature, and rapidly when the finely divided metal is heated and brought into contact with the mercury. Amalgams of silver and mercury in various proportions occur naturally; that called arquerite is crystalline and has a composition represented by the formula $AgHg_3$; other varieties approximate to the formulæ AgHg and Ag_2Hg_3.

The artificially prepared silver amalgam is sometimes soft and granular and sometimes crystalline. The union of the metals is attended with considerable contraction.

The other amalgams will be described under the heads of the several metals.

MERCUROUS OXIDE.

Formula Hg_2O. Molecular Weight 416.

History.—The existence of this compound was ascertained by the study of the difference between the solution obtained by dissolving mercury in nitric acid with and without the aid of heat. In 1775 Bergman showed that these solutions gave different precipitates with reagents, but it was not until a later period that this difference was ascribed to the different degrees of oxidation of the mercury.

Characters.—Mercurous oxide is a dark brown pulverulent substance insoluble in water; it is decomposed slowly by exposure to light, and readily when rubbed or warmed, into mercuric oxide and metallic mercury. As obtained by the action of caustic alkali upon calomel, it has a specific gravity of 8·95.

Mercurous oxide forms with acids a number of saline compounds in which the metal appears to be monovalent; the composition of the nitrate is represented by the formula $Hg_2 2NO_3$, that of the sulphate by the formula Hg_2SO_4. There are also a number of basic salts.

MERCURIC OXIDE.

Formula HgO. Molecular Weight 216.

History.—This substance was known to Geber, and it was prepared by him by heating mercury in contact with atmospheric air. Raymond Lully obtained it by heating mercuric nitrate; in 1774 Bayen observed that by mere heating it was converted into metallic mercury and a gas, and that the mercury thus obtained weighed less than the oxide operated upon. The discovery of oxygen by Priestley and the publication of Lavoisier's views on the nature of metallic oxides took place immediately after these important facts were made known.

Characters.—Mercuric oxide is either a bright red crystalline powder, or when prepared by precipitation from a mercuric salt, a pale orange yellow powder. Its specific gravity is 11·136. When heated its colour becomes darker and almost black, but on cooling it resumes its original tint. When more strongly heated it is decomposed into metallic mercury and oxygen gas; it is also decomposed to some extent when exposed to sunlight. The oxide obtained by precipitation is more readily decomposed than that obtained by heating the nitrate or by the oxidation of mercury, probably owing to the different states of aggregation.

Mercuric oxide is very sparingly soluble in water, and the solution has a strong metallic taste. Chlorine converts it into mercuric chloride with evolution of oxygen, at a high temperature, and at lower temperatures hypochlorous acid is also formed. Mercuric oxide combines with lime and baryta, forming soluble crystalline substances; it also combines with caustic alkalies and with ammonia. With acid oxides it forms saline compounds, many of which are crystallisable, but are decomposed by water unless there is excess of acid present. The composition of the sulphate is represented by the formula $HgSO_4$, that of the nitrate by the formula $Hg2NO_3$. There are also a number of basic salts.

Preparation.—Mercuric oxide may be prepared by adding caustic potash or soda, to a solution of mercuric chloride, or by gradually heating mercuric nitrate until nitrous vapour is no longer given off, and when thus prepared it is known as red precipitate. It is also formed by direct combination when mercury is kept for some

time at a temperature near the boiling point in contact with amospheric air until the whole of the metal is oxidised.

MERCUROUS CHLORIDE.

FORMULA Hg_2Cl_2. MOLECULAR WEIGHT 471.

History.—This substance was known under the name of *mercurius dulcis* at the early part of the seventeenth century, and had been previously obtained mixed in various proportions with mercuric chloride. Under the name of calomel (from καλὸς and μέλας) it was used medicinally, and it is said that this designation had reference to its efficacy in bilious disorders. The nature of the difference between this substance and mercuric chloride was not clearly ascertained until the time of H. Davy.

Occurrence.—Mercurous chloride occurs naturally as horn quicksilver, associated with cinnabar, but it is generally prepared artificially.

Characters.—Mercurous chloride in the form of horn quicksilver is either in prismatic crystals or granular masses of a dirty white colour. As prepared by sublimation, it is also crystalline or in fibrous masses; its density is 7·14. As obtained by precipitation from a solution of a mercurous salt, it is a heavy white powder with a slight tinge of yellow, tasteless, inodorous, and quite insoluble in water. When heated it does not melt, but at a red heat it volatilises without decomposition; by exposure to light it gradually acquires a grey colour.

Mercurous chloride is dissolved by nitric acid with evolution of nitrous vapour, and the solution contains mercuric chloride and nitrate. Sulphuric acid does not act upon it unless heated. By boiling with hydrochloric acid mercurous chloride is gradually converted into mercuric chloride and metallic mercury; the same change is more readily produced by solutions of the alkaline chlorides, and it takes place to a slight extent when mercurous chloride is boiled with water. Solutions of caustic alkali convert mercurous chloride into black mercurous oxide, and solution of ammonia also converts it into a black substance which is the chloride of dimercurosammonium NH_2Hg_2Cl.

A similar compound NH_3HgCl is formed when precipitated mercurous chloride is exposed to the action of dry ammonia at ordinary temperatures; the gas is absorbed, and the black powder formed gives off ammonia, when exposed to the air, leaving white mercurous chloride.

Preparation.—Mercurous chloride may be obtained by mixing a solution of sodium chloride with a warm dilute solution of mercurous nitrate; the chloride solution must be added in excess, and the precipitate well washed with boiling water. It is however generally prepared by sublimation; for this purpose mercuric chloride is rubbed with three-fourths of its weight of metallic mercury and some water and alcohol, until the globules of mercury entirely disappear and the mercuric chloride has been to a great extent converted into mercurous chloride:

$$\underset{275}{HgCl_2} + \underset{200}{Hg} = \underset{475}{Hg_2Cl_2}$$

The mixture is then sublimed in a glass vessel.

It may also be prepared by heating an intimate mixture of mercurous sulphate and sodium chloride until the mercurous chloride sublimes:

$$\underset{496}{Hg_2SO_4} + \underset{117}{2NaCl} = \underset{142}{Na_2SO_4} + \underset{471}{Hg_2Cl_2}$$

The mercurous sulphate is prepared for this purpose by rubbing mercuric sulphate with sufficient mercury to produce the alteration:

$$\underset{296}{HgSO_4} + \underset{200}{Hg} = \underset{496}{Hg_2SO_4}$$

The mercurous chloride obtained by sublimation in the form of a dense fibrous mass is powdered and thoroughly washed. Sometimes, in order to obtain the substance in a very fine powder, steam is injected into the vessel receiving the vapour of mercurous chloride, or the vapour is condensed in a large brick chamber. In both cases it is necessary to wash the product obtained in order to remove any mercuric chloride that may be mixed with it.

Use.—Mercurous chloride is used largely in medicine.

MERCURIC CHLORIDE.

FORMULA $HgCl_2$. MOLECULAR WEIGHT 271.

History.—This substance, commonly called corrosive sublimate, was well known to Geber and Albertus Magnus, and in the time of Basil Valentin it was an article of commerce under the name of *mercurius sublimatus*.

Characters.—Mercuric chloride is a colourless crystallisable substance. The specific gravity is 5·42. It melts at 265°, and boils at 295°, volatilising more readily than mercurous chloride. It has an acrid metallic taste and is very poisonous. It dissolves in water in the following proportions according to Poggiale:

	Temperature.		Quantity of Salt.
100 parts of water at	0°	dissolve	5·73
	20°		7·39
	40°		9·62
	60°		13·86
	80°		24·32
	100°		58·96

Mercuric chloride also dissolves in 2·5 times the weight of alcohol at the ordinary temperature, and in rather more than its own weight of boiling alcohol. Ether dissolves it almost in the same porportions.

Boiling hydrochloric acid dissolves mercuric chloride and appears to combine with it, forming a double salt $2HgCl_2$. HCl, which is decomposed by exposure to the air. Mercuric chloride combines with other chlorides in a similar manner. The compound with ammonium chloride $HgCl_2$, $2NH_4Cl.H_2O$ has long been known under the name of *sal alembroth*.

Mercuric chloride dissolves readily in nitric acid without alteration. It is not acted upon by sulphuric acid. When intimately mixed with metallic mercury, it is almost entirely converted into mercurous chloride; caustic alkalies precipitate mercuric oxide from a solution of mercuric chloride; solution of ammonia abstracts half the chlorine, and produces the substance known as white precipitate NH_2HgCl, according to the following equation:

$$HgCl_2 + 2NH_3 = NH_2HgCl + NH_4Cl.$$

The dry salt absorbs gaseous ammonia rapidly, and forms a substance having the composition $HgCl_2NH_3$ which can be distilled without separation of ammonia, but is decomposed by water.

Mercuric chloride combines with albumin, forming an insoluble white substance which does not putrefy when kept.

Preparation.—Mercuric chloride is formed by the direct combination of mercury and chlorine; by dissolving mercury with nitro-hydrochloric acid, containing a sufficient amount of hydrochloric acid, or by dissolving mercuric oxide in hydrochloric acid.

It is prepared on the large scale by sublimation from a mixture of mercuric sulphate and sodium chloride:

$$\underset{296}{HgSO_4} + \underset{117}{2NaCl} = \underset{142}{Na_2SO_4} + \underset{271}{HgCl_2}.$$

MERCURIC SULPHIDE.

FORMULA HgS. MOLECULAR WEIGHT 232.

History.—This substance in its natural form has been known from a very remote time, and was described under the name of *κιννάβαρι* by Theophrastus, who also speaks of its being made artificially, but it was often confounded with minium or red lead, and with the resin called dragons' blood. The production of this substance by combining sulphur with mercury was, however, distinctly described by Albertus Magnus, and in the time of Agricola cinnabar was made in this way at Venice. The black substance obtained by rubbing hot mercury with melted sulphur was first described by Turquet de Mayerne at the commencement of the seventeenth century, and in 1689 Harris prepared it by rubbing mercury with powdered sulphur. Its preparation from a solution of mercury by means of an alkaline sulphide was described by Jacobi in 1757, and under the name of *pulvis hypnoticus* it was used in medicine. The production of cinnabar by shaking mercury with a solution of sulphur in ammonia was described by Schulz in 1687, and in 1797 Kirchhoff discovered a method of

preparing it in this way. Up to a comparatively recent period, however, it was considered that the composition of the black substance was different from that of cinnabar, until Fuchs showed that the difference in colour was due to the state of aggregation.

Occurrence.—Mercuric sulphide occurs naturally as cinnabar, associated with metallic mercury and amalgam, disseminated throughout slaty or calcareous rocks which are not unfrequently bituminous: it constitutes the principal ore of mercury.

Characters.—Mercuric sulphide as it occurs naturally is either in the form of hexagonal prisms or fibrous compact masses. It has a dark red colour and considerable lustre. The specific gravity is 8·0 to 8·99. The powder has a fine scarlet colour. The artificially prepared substance known as vermilion is a very finely divided crystalline powder.

The amorphous sulphide obtained by precipitation is a black powder, and when heated in a close vessel it volatilises without melting, forming a crystalline sublimate.

The black amorphous sulphide obtained by precipitation is converted by contact with alkaline persulphides into the crystalline red sulphide. This change takes place slowly at the ordinary temperature and more rapidly by the aid of heat.

The crystalline sulphide acquires a dark colour when heated, but resumes the red colour on cooling, if the heat has not been sufficient to cause volatilisation.

When heated in contact with atmospheric air, mercuric sulphide is decomposed, the sulphur being converted into sulphurous oxide, and the mercury volatilised. Heated with caustic alkalis, alkaline earths, or alkaline carbonates, it is also decomposed, mercury being set free, as shown by the following equation:

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4.$$

Mercuric sulphide is decomposed by strong nitric acid with separation of sulphur; it is readily dissolved by nitro-hydrochloric acid, but is scarcely at all acted upon by dilute nitric acid; the amorphous substance is dissolved by potassium sulphide which combines with it, forming a crystallisable substance $HgSKS.5H_2O$, which is decomposed by water. Mercuric sulphide is decomposed when heated and rubbed with finely divided copper or iron.

Preparation.—The amorphous sulphide is formed when sulphuretted hydrogen is passed through a solution of a mercuric salt, or when mercury and sulphur are rubbed together for a considerable time; the product thus obtained was formerly known by the name of *Aethiops mineralis*, and it is entirely soluble in boiling caustic potash.

The crystalline sulphide, or vermilion, is prepared by subliming an intimate mixture of mercury or mercuric oxide and sulphur. When melted sulphur is mixed with 5 or 6 times its weight of mercury, and the mixture heated with constant stirring, till the sulphur begins to become thick, combination takes place suddenly with a crackling noise and evolution of heat and light. The substance thus obtained has a blackish-red colour, and consists partly of cinnabar with some amorphous sulphide, uncombined mercury and sulphur; when powdered and gradually heated to redness in a close vessel a sublimate of pure cinnabar is obtained.

The subliming vessels used for making cinnabar are earthen cylinders about 4 feet long, closed at one end and glazed inside; these are set vertically in a furnace so that the bottom can be heated to redness; the mixture of mercury and sulphur is thrown into each, and when the excess of sulphur has been driven off, the open ends of the cylinders are closed with cast-iron plates, upon which the sublimed cinnabar condenses.

Uses.—Mercuric sulphide is chiefly used in the form of vermilion as a pigment.

MERCUROUS SULPHATE.

Formula Hg_2SO_4. Molecular Weight 496.

This salt is prepared by heating sulphuric acid with excess of mercury until the whole is converted into a white powder, care being taken that the heat is not allowed to rise to the boiling point of the acid; the residue is then washed to remove free acid.

Mercurous sulphate is sparingly soluble in water, requiring 500 parts of cold water, and 300 parts of hot water for solution. It crystallises from the hot solution in rhombic prisms.

MERCURIC SULPHATE.

FORMULA $HgSO_4$. MOLECULAR WEIGHT 296.

This salt is prepared by heating mercury with rather more than its weight of sulphuric acid, until sulphurous oxide is no longer given off and a dry saline mass is formed:

$$\underset{200}{Hg} + \underset{196}{2H_2SO_4} = \underset{296}{HgSO_4} + \underset{64}{SO_2} + \underset{36}{2H_2O}.$$

Mercuric sulphate melts at a red heat, but is partially decomposed when volatilised; it is decomposed by water into an acid salt which dissolves, and an insoluble basic salt of a lemon-yellow colour, formerly known as turpeth mineral:

$$4HgSO_4 = HgSO_4 2SO_3 + HgSO_4 2HgO.$$

MERCUROUS NITRATE.

FORMULA $Hg_2 2NO_3$. MOLECULAR WEIGHT 524.

This salt is formed when moderately strong nitric acid is digested with an excess of mercury in the cold, and it is deposited in the form of crystals containing one molecule of water, which may be dissolved in a small proportion of water, but are decomposed by a larger proportion, forming an insoluble yellow precipitate of basic mercurous nitrate $Hg_2 2NO_3, Hg_2O, H_2O$; there are several other basic mercurous nitrates, some of which are soluble and are deposited in crystals from a hot solution of the neutral salt in contact with metallic mercury.

Mercurous nitrate forms double salts with barium, strontium, and lead nitrates, and the solution is decomposed by ammonia, yielding a black precipitate called Hahnemann's soluble mercury, the composition of which varies according to the conditions under which it is produced. (See p. 458.)

MERCURIC NITRATE.

FORMULA $Hg2NO_3$. MOLECULAR WEIGHT 324.

This salt is formed when mercuric oxide is dissolved in excess of nitric acid; by evaporating the solution at a gentle heat, a syrupy liquid is obtained, containing the salt in a hydrated state, and by exposing this liquid over sulphuric acid, it deposits crystals having the composition represented by the formula $2(Hg2NO_3)H_2O$.

Mercuric nitrate is readily decomposed by water with formation of a white precipitate consisting of a basic salt insoluble in water, and convertible into red mercuric oxide, by washing with large quantities of water. Another basic nitrate is formed when mercury is dissolved in boiling nitric acid, and it is deposited as the solution cools in needle-shaped crystals, consisting of $Hg2NO_3, HgO$. A solution of mercuric nitrate digested with excess of mercury yields mercurous nitrate.

Mercuric nitrate combines with mercuric cyanide, mercuric iodide, and argentic iodide, forming double salts which are crystallisable; also with mercuric phosphide and mercuric sulphide.

TIN.

Symbol Sn. Atomic Weight 118.

History.—It is at least tolerably certain that in the first century of our epoch this metal was indicated by the term *κασσίτερος*, and that it was the *plumbum candidum* or *album* mentioned by Pliny. Whatever may have been known of this metal prior to that time, it probably was not regarded as being essentially different from lead, which was termed by the Romans *plumbum nigrum*. The name *stannum* was used by Pliny to denote an alloy of lead, and it is only since the fourth century that this term has been used as the equivalent of *κασσίτερος* to denote tin. In Pliny's time the art of coating copper vessels with tin was known; the tinning of iron is mentioned by Agricola, but it appears to have been little known at that time, and it is commonly stated to have been discovered in Bohemia about the year 1620; a hundred years afterwards it was practised in England and somewhat later in France.

Occurrence.—Tin does not occur naturally in the metallic state, but chiefly in combination with oxygen, as cassiterite SnO_2, which is the principal source of this metal. It also occurs to some extent combined with sulphur, cuprous sulphide, and ferrous sulphide, or zinc sulphide, as stannine, or tin pyrites Cu_2S,FeS,SnS_2.

Characters.—Tin is a white metal closely resembling silver in appearance; its specific gravity is 7·29. When rubbed it has a peculiar smell. It is harder than lead, takes a high polish, and is very malleable; when bent it gives a crackling sound. It is sufficiently ductile to be drawn into wire when slightly warmed, but its tenacity is not much greater than that of lead.

Tin melts at from 222° to 237° without sensible volatilisation, but it boils at a white heat. When exposed to the atmosphere at the ordinary temperature it does not oxidise, but is soon tarnished by impure air, probably owing to the formation of sulphide on the surface. When heated and exposed to moist air, a film of oxide is formed on the surface. At a red heat it decomposes steam and is oxidised, while hydrogen is liberated. When melted in contact with atmospheric air the metal is oxidised, and at a full white heat it burns with a bright flame, stannic oxide being formed.

Tin is dissolved slowly by dilute hydrochloric acid, and rapidly by the strong acid with the aid of heat, stannous chloride being formed and hydrogen evolved; it is but little acted upon by dilute sulphuric acid, even when heat is applied, but the concentrated acid acts upon the metal and sulphurous oxide is produced. Strong nitric acid has no action upon tin, but dilute nitric acid acts violently and converts the metal into the insoluble form of stannic acid. Melted caustic alkalies oxidise and dissolve tin, melted alkaline nitrates have the same action. Tin combines readily with chlorine, bromine, sulphur, or phosphorus, when heated with these substances.

The tin of commerce is seldom quite pure, but generally contains either arsenic, lead, iron, or copper, in small proportions, sometimes antimony, zinc, bismuth, manganese, tungsten, molybdenum and gold.

Tin has a remarkable tendency to crystallise, and on washing the surface of the metal with warm dilute nitro-hydrochloric acid, the crystalline structure becomes apparent, owing to the unequal reflection of light from the faces of the crystals exposed by the action of the acid.

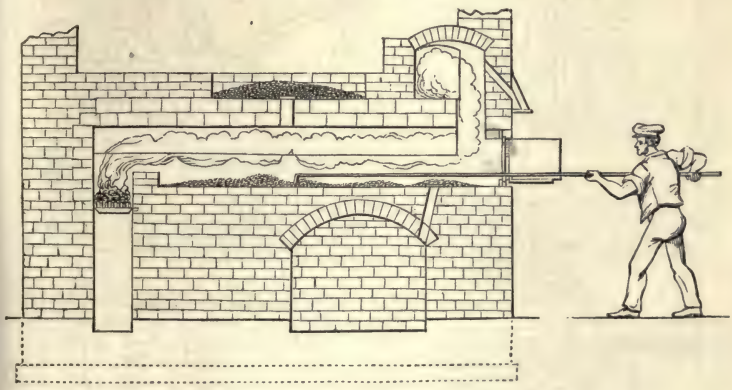
Preparation.—The only ore from which tin is extracted is cassiterite, or native stannic oxide, and as this mineral is generally associated with sulphuretted and arsenical compounds, the ore is subjected to several operations to purify it from these admixtures before the oxide is reduced. To a great extent these preliminary operations are mechanical, and consist in first washing the finely divided ore with water so as to separate those impurities which are less dense than stannic oxide, and by reason of the great density of this substance its concentration and purification by this means can be carried to a considerable extent. The denser impurities which remain mixed with the stannic oxide after washing consist of metallic arsenides and sulphides, for

the separation of which the washed material is next roasted in contact with atmospheric air, by which means sulphur and arsenic are oxidised and separated, while the metals combined with these substances are converted into oxides or soluble sulphates; the roasted material is then washed again with water to dissolve out the soluble salts and separate the insoluble oxides, which are inferior in density to stannic oxide. The residue left after this treatment of the ore is called black tin.

The smelting of tin ore thus prepared is effected either in reverberatory furnaces or shaft furnaces, by heating the oxide with coal or charcoal and lime, and the chemical change involved in this operation consists chiefly in the reduction of the stannic oxide by the carbonaceous material used as fuel. The temperature requisite for this reduction is very high, and sufficient to effect the reduction of other metallic oxides present in the ore, as well as to determine the combination of stannic oxide with silica; so that while the reduced metal thus obtained is impure, and requires refining, the slag or scoria produced still contains some tin, and is again smelted in a similar manner.

Since tin ore frequently contains a considerable amount of arsenic, the operation of roasting is a necessary part of the preliminary treatment. In Cornwall it is conducted in furnaces of the kind represented in vertical section and plan by figs. 363 and 364.

Fig. 363.



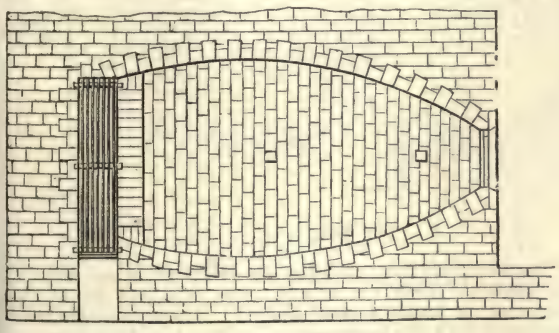


Fig. 364.

In working this furnace the bed is supplied with fresh ore through an opening in the arch by which it is covered, and the ore lying upon the top of the arch is dried by the waste heat. Close to the working door, which is at the end of the bed opposite to the fire, there is an ascending flue by which the arsenical vapour passes away into an arched tunnel of considerable length where the arsenous oxide is condensed and deposited. While this operation is going on the finely divided ore on the bed of the furnace requires to be frequently stirred in order to facilitate the oxidation of the arsenical and sulphur compounds, by exposing fresh surfaces; and mechanical arrangements have been devised for the purpose of effecting this.

One of these contrivances which has been extensively used is known as Brunton's Calciner, and its construction is represented by fig. 365.

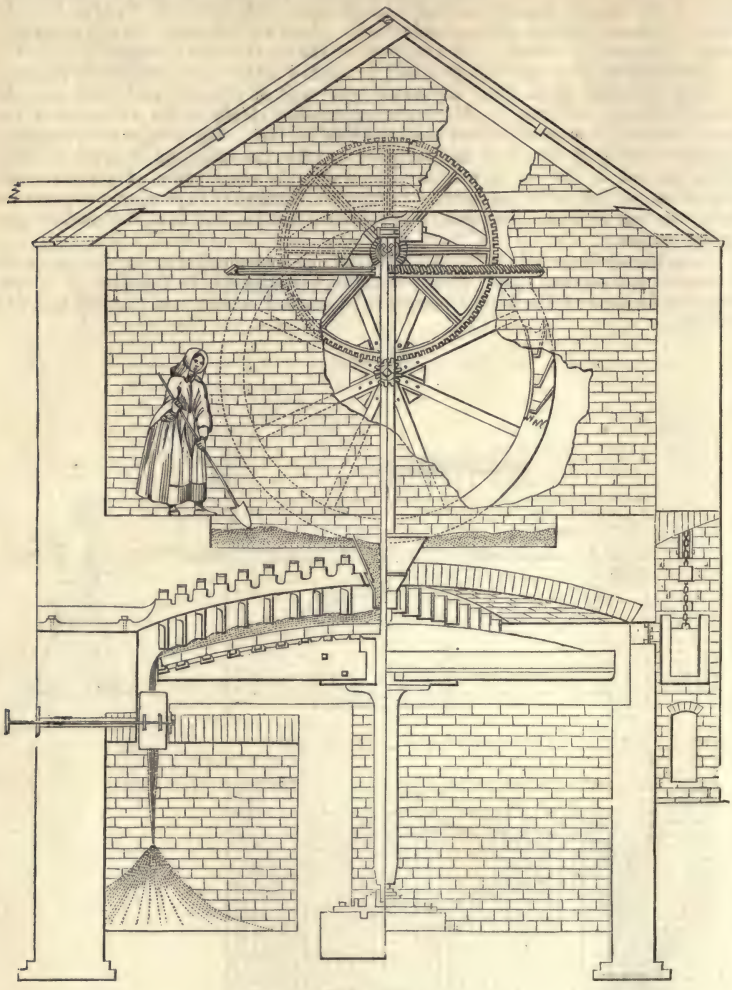


Fig. 365.

It consists of a circular table constructed of fire bricks set in an iron frame attached to a vertical shaft, the lower end of which rests on a step, and by means of toothed wheels the table is made to revolve slowly. Above the table is a flat arch or dome communicating with two furnaces, and the flame from them passes over the surface of the table. At the centre of the dome is a hopper through which the finely divided ore is fed on to the table, and to the top of the dome are attached cast-iron frames fitted with blades, which stir up the ore as it is carried round on the table, so that by the time the ore has passed from the centre of the table to the circumference it has been sufficiently roasted, and then it falls down through an aperture in the brick-work into a vault beneath.

Another kind of calciner is that of Messrs. Oxland and Hocking, in which the ore is exposed to the action of flame and hot air from a furnace, in a long iron tube supported in an inclined position and made to revolve on its axis by toothed wheels. The lower end of this tube communicates with a furnace, and likewise with a

chamber into which the roasted ore falls after having slowly travelled down the entire length of the tube. The upper end of the tube is connected with condensing chambers into which the products of combustion from the furnace pass, together with the arsenical and sulphurous vapour given off from the ore in roasting. The interior of the iron tube is lined with fire brick in such a manner as to form projecting ridges parallel with the axis of the tube; in this way the ore is raised as the tube revolves, and is then shot off the ridges in a shower.

Tin ore sometimes contains a considerable amount of the mineral called wolfram, which consists of ferrous tungstate and manganous tungstate, and it is desirable to separate this substance before smelting the ore; this cannot be done by washing, since wolfram has nearly the same density as stannic oxide, and the ordinary calcination also has little effect upon it. Oxland has devised a method of separation which consists in converting the tungstic oxide of the wolfram into sodium tungstate, which is soluble in water and can be washed out, while the iron and manganese oxides separated can be got rid of by washing. For this purpose the ore is mixed with rather more soda ash than is sufficient to form sodium tungstate by acting upon the wolfram present. This mixture is then heated upon the bed of a reverberatory furnace until it becomes red hot and has a semi-liquid appearance. Meanwhile the mass is well stirred, and after two or three hours it is drawn from the furnace: when cold it is lixiviated with water until the soluble portion is extracted. The residue is then washed with water so as to float off the oxides resulting from the decomposition of the wolfram, and leave the heavier stannic oxide ready for reduction.

Smelting in Reverberatory Furnaces.—This plan is now generally adopted in Cornwall, and the furnaces used for the purpose are represented by figs. 366 and 367. The bed (*f*) is slightly hollowed, and the fire bridge (*c*) by which it is separated from the fireplace (*b*) is provided with an air channel (*i*) extending also under the bed of the working chamber to prevent injury by too great heating. The charging door (*d*) is placed on one side of the bed, and at the opposite side is a tapping hole (*g*), by which the reduced metal can be drawn off into the basins (*k k*). The working door (*e*) is placed at the end of the bed, and the gaseous products pass off through the flue (*l*) into a chimney (*m*) at the side.

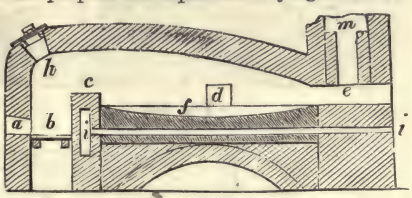


Fig. 366.

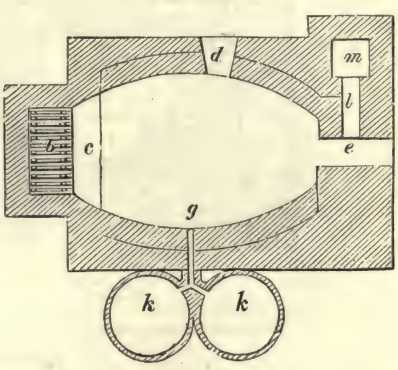


Fig. 367.

The material to be smelted, which should contain from 60 to 65 per cent. of tin, is well mixed with about one fifth its weight of small coal, some slaked lime and fluor spar, sometimes also with a little sodium chloride; the mixture is slightly damped with water before it is charged into the furnace, and after about five hours, when the heat has been raised to a sufficient degree, the mass is well stirred with a rabble to facilitate the separation of the reduced metal from the slag which is drawn out through the door (*e*). The metal and some liquid vitreous slag are then run off through the tap hole (*g*) into one of the basins (*k k*) where the melted slag is skimmed off.

The metallic tin thus obtained is still impure, and it is refined by gradually heating it in a reverberatory furnace of the same construction as fig. 366 until the tin melts and runs down upon the hearth, leaving a less fusible mixture of tin, iron, arsenic, etc. By opening the tap hole the melted metal is drawn into one of the basins (*k k*), under which there is a fire kept up sufficient to retain the metal in the liquid state; it is stirred with a piece of green wood for several hours, and the dross formed meanwhile is skimmed off the surface.

Another mode of refining the tin is to lift the liquid metal in ladles and pour it back from a considerable height into the pot. In either case, when the formation of dross has ceased, the metal is ladled out into moulds.

Smelting in Shaft Furnaces.—This method was formerly adopted in Cornwall, but has now been superseded by the use of reverberatory furnaces; it is however, still followed in Saxony and Bohemia. The furnaces used at Altenberg are represented by figs. 368 and 369. They are constructed of rough masonry (*a a*) lined with refractory materials (*b b b*), and the front wall (*c*) is supported upon a bar of iron, so as to leave an opening (*h*) called the eye, through which the melted contents of the furnace are run out into the fore hearth (*i*), formed of stone blocks (*k*) with a lining of loam (*l*), and kept in position by the iron plate (*p*); the channel (*m*) connects the fore hearth with another hemispherical receptacle (*n*) made of cast iron or stone, lined with loam and furnished with a fireplace for keeping the contents melted. At one side of the fore hearth provision is made for running the slag over the wall (*q*) on to a sloping iron plate (*o*), and then into the tank (*r*) containing water. The sole (*f*) of the furnace slopes from the back to the upper level of the fore hearth (*i*) and the melted products flow through the eye (*h*) into the fore hearth. The blast tuyere is inserted through the opening (*g*).

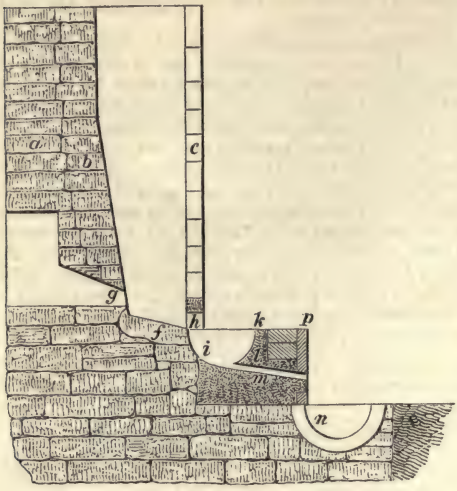


Fig. 368.

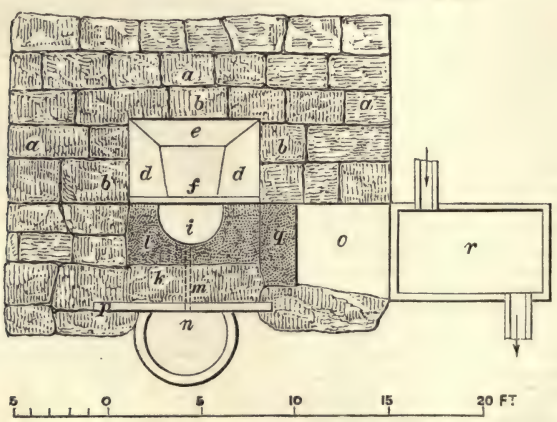


Fig. 369.

The height of the furnace shaft depends very much on the amount of iron in the ore, varying from seven to ten feet, the lower shaft being used in the smelting of highly ferruginous ores. Such ores frequently give rise to the production of deposits of the following composition:

Iron	61·52	62·60
Tin	30·50	31·43
Arsenic	1·45	—
Tungsten	0·90	1·60
Carbon, Silica, and Alumina	4·41	2·40
	98·78	98·03

The tin ores worked in shaft furnaces in Saxony and Bohemia are generally impure, and according to the nature of the substances they contain different materials must

be used as fluxes. Ores containing much ferric oxide are mixed with quartz, or other silicious substances, while silicious ores are mixed with lime, and ores containing wolfram are also mixed with lime. The proportion of lime should not be more than sufficient to render the slag moderately fusible, since an excess would cause loss of tin by the formation of calcium stannate.

The slag formed in smelting tin ore consists chiefly of ferrous silicate, together with some stannous silicate, and that portion which is drawn out before running off the melted products consists of a mixture of unburnt coal and other substances with metallic tin: this is crushed, washed, and again smelted.

The composition of the slag produced in reverberatory furnaces at Poullaouen is as follows, according to Berthier:—

Silica	41·30	40·00
Ferrous oxide	20·50	20·30
Manganous oxide	11·40	11·10
Alumina	12·80	9·60
Lime	3·90	3·60
Magnesia	0·80	1·00
Stannous oxide	9·00	8·40
	99·70	94·00

The slag produced in smelting tin ore in shaft furnaces has the following composition:

	Wallach	Berthier		Lampadius
Silica	24·06	16·0	27·5	5·81
Alumina	9·00	2·4	8·5	18·14
Ferric oxide	20·75	41·5	48·2	39·51
Manganous oxide	5·64	1·7	1·5	1·34
Lime	3·58	3·7	3·4	—
Magnesia	0·37	1·7	1·6	—
Stannic oxide	10·41	—	—	12·13
Stannous oxide	—	32·0	6·3	—
Tungstic oxide	24·33	1·0	3·0	—
Tin	—	—	—	21·20
	98·14	100·	100·	98·13

The residue left in the refining of the metal obtained in the first smelting has the following composition:—

	Berthier	Phillips
Iron	55·6	62·50
Tin	36·2	17·25
Cobalt	4·0	—
Arsenic	4·2	19·02
Sulphur	—	1·26
	100·0	100·03

Uses.—Tin is employed for making various kinds of vessels for domestic use and other purposes, and is often alloyed with some lead in order to render it less brittle. It is also used in the form of very thin sheets, called tin foil, for wrapping articles of food, etc.; looking-glasses also are coated with tin foil, which is then converted into an amalgam with mercury, and thus made to adhere to the glass and present a very brilliant reflecting surface. Tin is also extensively employed for coating sheet iron and rendering it more suitable for use in the form of domestic vessels, etc., by protecting the iron from atmospheric oxidation. Sheet iron so coated is commonly called tin plate; it is prepared by dipping sheets of iron, well cleansed at the surface by means of acid, into melted tin until the surface is sufficiently coated with tin.

Compounds.—Tin forms two well-defined series of compounds; it is tetravalent in the stannic compounds, and divalent in the stannous compounds. In many respects the compounds of tin present considerable analogy with those of silicon and titanium. Stannous oxide SnO is a moderately strong base, forming definite saline compounds with acid oxides; stannic oxide SnO_2 is an acid oxide which forms saline compounds with water and basic oxides; the hydrogen salt H_2SnO_3 is called stannic acid. The oxide Sn_2O_3 is probably a compound of this kind in which

stannous oxide is the base combined with stannic oxide. There are in the same way three compounds of tin with chlorine, the dichloride $SnCl_2$ corresponding to stannous oxide, the tetrachloride $SnCl_4$ corresponding to stannic oxide, and a sesquichloride Sn_2Cl_6, which is probably a compound of stannic chloride with stannous chloride, analogous to the salts formed by the combination of stannic chloride with potassium chloride, etc., called **chlorostannates**, in which stannic chloride acts the part of an acid. The compounds of tin with fluorine, with bromine, and with iodine correspond to stannous and stannic chlorides; stannic fluoride, however, has not been obtained in a separate state, but only in combination with other fluorides corresponding to potassium fluoride, in the form of **fluostannates**, which are analogous in constitution to the stannates, but contain fluorine in the place of oxygen; the composition of the barium salt is represented by the formula $BaF_2SnF_4 = BaSnF_6$. These compounds are analogous to the fluosilicates, fluotitanates, and fluoborates (see p. 184). The compounds of tin with sulphur correspond to the oxides, and stannic sulphide SnS_2 combines with basic sulphides, forming a series of compounds called **sulphostannates** in which stannic sulphide acts the part of an acid. These salts are also analogous to stannates, but contain sulphur in place of oxygen.

Tin also forms a number of compounds with alcohol radicles.

Tin unites with most other metals when melted with them, forming alloys which are generally hard and ductile. In some instances a very small proportion of tin modifies the characters of other metals very considerably.

The alloys of tin with zinc are harder than tin but softer than zinc; they are also less malleable than tin; that containing one-twelfth part of tin is used for making foil that is employed as a substitute for silver leaf. The alloy containing 6 molecular proportions of tin to one of zinc solidifies at 204°, and the alloys of these metals in different proportions separate, when gradually cooled, into this alloy and another which solidifies at a higher temperature.

The alloys of lead with tin are harder than tin, rather darker in colour, and when bent they do not give the crackling sound characteristic of tin. The **solder** used for various purposes consists of lead and tin in the following proportions:

	Tin	Lead	Melting point
Fine solder	2	1	340°
Common solder	1	1	370°
Coarse solder Sealed solder	1	2	441°

Pewter generally consists of tin alloyed with one-fourth its weight of lead, but zinc or other metals are sometimes added, and the better kind contains a larger proportion of tin. This alloy is remarkable in not being acted upon by acid liquids in the same way that lead is, and on this account it can be used for domestic utensils when the proportion of tin is not less than 82 per cent. Alloys of tin and lead in various proportions differ considerably in the melting point, as shown in the following table, and they are used as baths, for tempering articles made of steel:

Lead	Tin	Melting point	
14	8	213°·4	used for tempering lancets
15	8	221°	,, ,, surgical instruments
16	8	225°	,, ,, razors
17	8	240°	,, ,, penknives
28	8	257°	,, ,, shears
38	8	262°	,, ,, hatchets, planes, etc.
60	8	275°	,, ,, table knives, scissors, etc.
96	8	284°	,, ,, swords and watch springs
100	8	289°	,, ,, augurs, saws, and strong springs

The alloys of tin and lead are remarkable for the readiness with which they undergo oxidation when heated in contact with atmospheric air. The alloy containing 20 or 25 per cent. of tin burns like charcoal at a red heat. This oxidation appears to be promoted by the combination of the stannic oxide with the lead oxide. (See Enamel, p. 331.)

The alloys known by the names of **bronze**, **gun metal**, **bell metal**, consist either entirely or chiefly of tin and copper, and their characters vary according to the relative proportions of the two metals, as shown in the following table by Mallet:

	Copper	Tin	Specific gravity	Colour	Tenacity	Hardness
1	100·	—	8·607	—	24·6	10
2	84·29	15·71	8·561	reddish yellow	16·1	8
3	82·81	17·19	8·462		15·2	5
4	81·10	18·90	8·459	yellowish red	17·7	4
5	78·97	21·03	8·728		13·6	3
6	76·29	23·71	8·750	pale red	9·7	2
7	72·80	27·20	8·575		4·9	1
8	68·21	31·79	8·400	ash grey	0·7	6
9	61·69	38·31	8·539	dark grey	0·5	7
10	51·75	48·25	8·416	greyish white	1·7	9
11	34·92	65·08	8·056		1·4	11
12	21·15	78·85	7·389	white	3·9	12
13	15·17	84·83	7.447		3·1	13
14	11·82	88·18	7·472		3·1	14
15	9·68	90·32	7·442		2·5	15
16	0·	100·	7·291	—	2·7	16

The alloy containing only a small proportion of tin is much harder than copper, and when hammered it becomes still harder and brittle; it is however softened by heating to redness and sudden cooling; when slowly cooled it becomes hard. The alloy used as gun metal and for castings contains from 8 to 19 per cent. of tin; when the tin amounts to 21 per cent. the alloy is very hard and suitable for the bearings of machinery; the alloys with somewhat larger amounts of tin are used for casting bells, and some zinc and lead are often mixed with the alloy. In proportion as the amount of tin is augmented the alloys become whiter and more brilliant; that used for the mirrors of reflecting telescopes, under the names of speculum metal, contains about 33 per cent. of tin; it is very hard, of a steel colour, and takes a high polish.

The alloys of tin with silver are nearly as white as silver. They are brittle and generally hard, that containing 20 per cent. of tin being as hard as bronze.

Tin unites readily with mercury, even at the ordinary temperature, forming a brittle granular amalgam if the proportion of mercury is not too large. The metallic reflecting surface on plate-glass mirrors consists of an amalgam of tin.

The other alloys of tin will be described under the heads of the several metals.

STANNOUS OXIDE.

Formula SnO. Molecular Weight 134.

History.—The distinction between the oxides of tin was not recognised until the latter end of the last century.

Characters.—Stannous oxide is either black, greenish brown, or red, according to the way in which it is prepared. At the ordinary temperature it is not oxidised by contact with atmospheric air, but when heated it is rapidly converted into stannic oxide. It is reduced by hydrogen or carbon at a red heat. Chlorine converts it into stannic chloride and stannic oxide; when heated with sulphur it yields stannic sulphide and sulphurous oxide; by boiling caustic alkali it is converted into alkaline stannate, with separation of metallic tin; it is dissolved by acids, forming stannous salts.

Stannous hydrate $Sn_2H_2O_3$, as obtained by mixing a solution of a stannous salt with an alkaline carbonate, is a white precipitate readily soluble in acids and fixed alkalies, but insoluble in solution of ammonia. When boiled with water it is converted into anhydrous stannous oxide, and by exposure to the air it is oxidised and converted into stannic hydrate.

Preparation.—Stannous oxide may be prepared either by drying the hydrate out of contact with air at a temperature not exceeding 80° or by boiling the hydrate with some caustic potash or soda insufficient to dissolve it. It may also be prepared by heating stannous oxalate out of contact with air. The red modification is prepared by evaporating a dilute solution of ammonium chloride in which stannous hydrate oxide is suspended. As soon as the chloride crystallises, the hydrate is converted into anhydrous oxide in the form of a cinnabar red powder.

STANNIC OXIDE.

FORMULA SnO_2. MOLECULAR WEIGHT 150.

History.—The true composition of this substance was not determined until the early part of the present century, and it was shown by Berzelius that the product obtained by oxidising tin with nitric acid had the same composition as that precipitated from stannic chloride by an alkali.

Occurrence.—Stannic oxide occurs naturally as cassiterite or tin stone, either as crystals and lumps imbedded in granite and other crystalline rocks, or in the form of pebbles in alluvial deposits.

Characters.—Stannic oxide in the crystalline state, as it occurs naturally, forms quadratic prisms which are colourless when pure, but are more frequently yellow, grey, brown, or black, owing to the presence of other substances. In the amorphous state, stannic oxide is a white or yellowish-white powder, which acquires a slight brown tinge when heated, but becomes white again on cooling. The specific gravity is from 6·6 to 6·9. It is extremely hard, melts only at a very high temperature, and is not acted upon even by concentrated acids; when melted with acid potassium sulphate it is dissolved, but separates completely on treating the melted mass with water; it is not dissolved when melted with alkaline carbonates, but when melted with caustic alkali it is converted into a soluble stannate; by ignition in contact with chlorine it is converted into stannic chloride; heated to redness with hydrogen, carbonic oxide, carbon, or carburetted gases, it is reduced to the metallic state.

Stannic oxide forms two compounds with water SnO_2H_2O and $Sn_5O_{10}5H_2O$, which represent two series of salts called respectively stannates and metastannates, the stannic hydrates being the hydrogen salts of those two series, or stannic acid H_2SnO_3 and metastannic acid $H_{10}Sn_5O_{15}$. The whole of the hydrogen in stannic acid can be replaced by metals, but only one-fifth of the hydrogen in metastannic acid can be thus replaced.

Stannic acid, as obtained by drying the precipitate formed on adding an acid to the solution of an alkaline stannate, has the form of translucent lumps like gum, and it reddens litmus paper; it is dissolved by hydrochloric acid, forming stannic chloride, and by oxyacids, forming stannic salts, which are very unstable. The sulphate $Sn2SO_4$ is an uncrystallisable syrupy liquid having a strong acid reaction; it is decomposed by water.

Potassium stannate K_2SnO_3 is a very soluble salt, crystallising in rhombic prisms containing 3 or 4 molecules of water; it is insoluble in alcohol, but dissolves in less than its weight of cold water; the solution has a specific gravity of 1·627.

Sodium stannate Na_2SnO_3 is less soluble than the potassium salt, requiring rather more than one and a half times its weight of water for solution. It crystallises in hexagonal plates containing 3 molecules of water. It is less soluble in warm water than in cold water.

The calcium, barium, and strontium stannates are obtained by boiling the corresponding hydrates or carbonates with a solution of sodium stannate, or by heating a mixture of natural stannic oxide and the respective nitrates to a high temperature in a reverberatory furnace.

Cupric stannate $CuSnO_3$ is an insoluble substance of a green colour obtained by mixing a solution of tin in nitro-hydrochloric acid with cupric sulphate and adding excess of caustic soda. It is used as a pigment.

Metastannic acid $H_{10}Sn_5O_{15}$ is a white crystalline powder insoluble in water and in nitric acid; it unites with hydrochloric acid and with sulphuric acid, but without dissolving; the compound with hydrochloric acid dissolves in pure water, but is again precipitated on the addition of strong hydrochloric acid; the compound with sulphuric acid is decomposed by water and all the sulphuric acid is extracted. When metastannic acid is heated with hydrochloric acid it is gradually converted into stannic chloride, and when melted with caustic alkali it is converted into stannic acid.

Metastannic acid dissolves slowly in solution of caustic alkalies, and when the solution is exposed to the air, it is again precipitated as carbonic dioxide is absorbed or on the addition of an acid. The precipitate thus produced is insoluble in nitric acid, but soluble in ammonia, while the acid formed by the action of nitric acid upon tin is insoluble in ammonia.

Potassium metastannate $K_2H_8Sn_5O_{15}$ is a gummy uncrystallisable substance with a strong alkaline reaction; it is soluble in water.

Sodium metastannate $Na_2H_8Sn_5O_{15}$ is a crystalline substance soluble in water, but decomposed when the solution is heated, and on boiling the whole of the metastannic acid is deposited.

Stannous metastannate $SnH_8Sn_5O_{15}$ is a yellow substance insoluble in water formed by placing metastannic acid in contact with stannous chloride. When heated it gives off water and becomes brown at 140°. By contact with atmospheric air and by the action of nitric acid it is converted into metastannic acid.

Preparation.—Stannic oxide is prepared by heating metallic tin for some time in contact with atmospheric air. The stannates are prepared by dissolving stannic hydrate in alkaline solutions; by melting stannic oxide together with basic oxides, or by boiling the solution of a soluble stannate with basic oxides. The sodium salt is prepared on the large scale by melting tin ore with sodium hydrate, nitrate, chloride, or sulphide; also by boiling the ore with caustic soda or by melting metallic tin with a mixture of sodium carbonate and sodium nitrate. Tin containing lead can be used for this purpose, or waste cuttings of tinned iron instead of pure tin.

Uses.—Stannic oxide is used in a finely divided state, under the name of putty powder, for polishing metals; it is also used in the production of enamel and opaque glass. In the state of sodium stannate it is used in calico printing as a mordant or preparing salt; when the dilute solution of this salt is brought into contact with the fibres of the fabric to be dyed, stannic hydrate is deposited upon them.

STANNOUS CHLORIDE.

Formula $SnCl_2$. Molecular Weight 189.

History.—The difference between the solution of tin in hydrochloric acid and that obtained by dissolving tin in nitro-hydrochloric acid was first ascertained by Pelletier in 1792.

Characters.—Stannous chloride is a translucent, almost colourless substance having a fatty lustre; it melts at 250°, boils near a red heat, and can be distilled; when heated in contact with atmospheric air it is decomposed, giving off stannic chloride, while stannic oxide is formed. It absorbs dry ammonia, and when heated with it forms the compound $SnCl_2NH_3$. Stannous chloride combines with water, forming a hydrate which is soluble in water and crystallises in large prisms, containing 2 molecules of water, commonly known as tin salt. This substance when heated gives off water and hydrochloric acid, and is converted into stannous chloride and stannous oxide. The crystallised salt dissolves completely in a small proportion of water free from atmospheric air, but a large proportion of water causes decomposition of some portion, and hydrated stannous oxychloride $SnOSnCl_2 2H_2O$ is deposited as a white precipitate, while hydrochloric acid is formed:

$$2SnCl_2 + H_2O = SnOSnCl_2 + 2HCl.$$

The clear solution becomes turbid when exposed to the air, oxychloride being deposited and stannic chloride formed by oxidation:

$$3SnCl_2 + O = SnOSnCl_2 + SnCl_4.$$

The decomposition may be prevented in either case by adding some hydrochloric acid, tartaric acid or ammonium chloride to the solution. The crystals decompose in the same manner when exposed to the air; they are also decomposed by cold sulphuric acid, and when heated with sulphuric acid some hydrochloric acid is given off with sulphurous acid and sulphuretted hydrogen, while stannic sulphate is formed.

Stannous chloride combines with several other chlorides, forming saline compounds called chlorostannites, in which the stannous chloride acts the part of an acid. The ammonium salt $2NH_4Cl.SnCl_2$ is soluble in water and forms crystals which are sometimes anhydrous and sometimes contain two molecules of water. The solution becomes cloudy on boiling, but is not altered by exposure to the air. The composition of the barium and strontium salts is represented by the formulæ $BaCl_2SnCl_2 4H_2O$ and $SrCl_2SnCl_2 4H_2O$.

Stannous chloride is readily converted into stannic chloride, either in the dry state by direct combination with chlorine, or in solution when mixed with any substance capable of giving up chlorine or oxygen, such as hypochlorous acid, nitric acid, chromic acid, and arsenic acid, or ferric, manganic, and cupric salts.

Preparation.—The anhydrous salt is prepared by heating tin in hydrochloric acid gas, or by heating the hydrated salt gradually until the water has been driven off; and then raising the heat sufficiently to distil off the chloride.

The hydrated salt is prepared by dissolving tin in hydrochloric acid. Copper vessels are used for the purpose, and they are not acted upon so long as some of the

tin remains undissolved. When the acid is fully saturated with tin the liquid is evaporated and left to crystallise.

Uses.—Stannous chloride is extensively used as a mordant in dyeing and calico printing; also as an antichlor and as a reagent in volumetric analysis.

STANNIC CHLORIDE.

FORMULA $SnCl_4$. MOLECULAR WEIGHT 260.

History.—This substance was formerly known in the anhydrous state as the *spiritus fumans* of Libavius. In 1770 Demachy observed that when mixed with a small quantity of water it solidified to a soft crystalline fusible mass called butter of tin.

The solution obtained by dissolving tin with nitro-hydrochloric acid has been known since 1630, when Drebbel discovered its use for dyeing.

Characters.—Stannic chloride is a colourless mobile liquid; its specific gravity is 2·234; it gives off dense white fumes when exposed to the air and is very caustic; it boils at 115°, and distils without alteration. When heated with a small quantity of water in a sealed tube it is decomposed and converted into stannic oxide. It absorbs water from the air and combines with it, forming a crystalline hydrate $SnCl_4 3H_2O$ which dissolves in water, and the solution when evaporated yields crystals containing 5 molecules of water. Stannic chloride is decomposed when the solution is largely diluted with water, and stannic acid, or metastannic acid, is precipitated. The solution of stannic chloride is decomposed when mixed with a solution of alkaline sulphate, and stannic hydrate is precipitated, while alkaline chloride and acid sulphate remain in solution.

The solution of stannic chloride dissolves stannous oxide, forming stannous chloride, which crystallises with 4 molecules of water when the solution is evaporated, and the liquid contains stannic hydrate dissolved in stannic chloride:

$$2SnCl_4 + 2SnO + H_2O = 2SnCl_2 + H_2SnO_3 + SnCl_4.$$

With a larger proportion of stannous oxide, stannic oxide separates in the hydrated state, and the liquid contains stannous chloride:

$$SnCl_4 + 2SnO = SnO_2 + 2SnCl_2.$$

Stannic chloride dissolves crystalline sulphur, but not amorphous sulphur; from the hot saturated solution sulphur crystallises in rhombic prisms. It also dissolves phosphorus and iodine; it mixes in all proportions with bromine and carbon bisulphide. It absorbs ammonia and forms the compound $SnCl_4 2NH_3$ which sublimes without decomposition and after sublimation is soluble in water. Vapour of sulphuric oxide is also absorbed by stannic chloride, forming a solid mass.

Sulphuretted hydrogen is absorbed by stannic chloride, and some hydrochloric acid is given off, while stannic sulphide is formed, which combines with part of the stannic chloride forming a reddish-yellow liquid:

$$3SnCl_4 + 2H_2S = SnS_2 2SnCl_4 + 4HCl.$$

Stannic chloride combines with sulphur tetrachloride, forming a yellow crystalline substance $SnCl_4 2SCl_4$; with phosphorus pentachloride, forming a white crystalline substance $SnCl_4 PCl_5$; with phosphorus oxychloride, forming a volatile crystallisable substance $SnCl_4 POCl_3$, and with phosphuretted hydrogen $3SnCl_4 2PH_3$.

Stannic chloride combines with alkaline chlorides, forming saline compounds called chlorostannates, which correspond to the stannates, but contain chlorine in place of oxygen, and the stannic chloride acts the part of an acid. The ammonium salt $2NH_4Cl . SnCl_4$ is a crystalline powder, soluble in three times its weight of water. The concentrated solution is not decomposed by boiling, but a dilute solution deposits stannic hydrate. This salt is used as a mordant in calico-printing under the name of pink salt, since the stannic hydrate separated by heating a dilute solution readily combines with colouring substances, and renders them insoluble; it is prepared by mixing concentrated solutions of the two chlorides in proper proportions. The potassium salt $2K_2Cl . SnCl_4$ is soluble in water, crystallisable, and permanent in the air. The sodium, calcium, magnesium, barium, and strontium salts are analogous.

Preparation.—The anhydrous substance is prepared by heating metallic tin or stannous chloride in contact with dry chlorine, or by distilling a mixture of tin filings

with four times the weight of mercuric chloride. The hydrated salt known as butter of tin is obtained by mixing anhydrous stannic chloride with one third its weight of water; by dissolving this substance in water and crystallising, the pentahydrate $SnCl_4 5H_2O$ is obtained.

An impure stannic chloride, known as nitromuriate of tin, is prepared by dissolving tin in nitrohydrochloric acid or a mixture of nitric acid and ammonium chloride.

Uses.—Stannic chloride is used chiefly by dyers, either in solution or in the form of pink salt, for brightening and fixing red colours.

STANNOUS SULPHIDE.

Formula SnS. Molecular Weight 150.

History.—The compound obtained by melting tin with sulphur is mentioned by Kunkel, but so very vaguely that it is uncertain whether he was really acquainted with this substance.

Characters.—Stannous sulphide is either a dark lead-coloured crystalline mass, or a brownish black amorphous powder. The specific gravity is from 4·8 to 5·2. It melts less readily than tin, and in the compact state is tough and difficult to powder. It is soluble in melted tin; when boiled with hydrochloric acid it is decomposed and sulphuretted hydrogen is given off; it is slowly oxidised when heated with nitric acid; chlorine gas converts it into stannic chloride and the compound of that substance with sulphur tetrachloride; when heated in contact with hydrogen the tin is slowly reduced to the metallic state, and when melted with potassium cyanide, tin is reduced, while potassium sulphocyanate is formed.

Stannous sulphide is but slightly dissolved by ammonium sulphide solution, but solutions of alkaline polysulphides dissolve it readily and convert it into stannic sulphide.

STANNIC SULPHIDE.

Formula SnS_2. Molecular Weight 182.

History.—This substance was known in the eighteenth century as *aurum musivum*, or mosaic gold, and its preparation was described in 1771 by Peter Woulf; but its composition was not correctly ascertained until 1812, when Davy and Berzelius showed that it did not contain oxygen.

Occurrence.—Stannic sulphide occurs naturally in combination with cuprous sulphide, ferrous sulphide and zinc sulphide, as stannine or tin pyrites, a mineral which is sometimes associated with tin ore.

Characters.—Stannic sulphide is a yellowish substance which in the crystalline state forms soft golden yellow laminæ, having a metallic lustre, and resembling bronze powder; in the amorphous state it is a yellowish brown powder. The specific gravity varies from 4·4 to 4·6. Stannic sulphide sublimes when heated in a close vessel, but is partly decomposed into sulphur and stannous sulphide. Heated in contact with atmospheric air it is oxidised, yielding stannic oxide and sulphurous oxide. In contact with chlorine it forms a brown liquid, from which crystals of the compound $SnCl_4 2SCl_4$ separate after some time. Heated with iodine it yields a dark yellow volatilisable substance $SnSI_2SI_2$, and the same substance is formed by boiling the amorphous sulphide with alcoholic solution of iodine.

Stannic sulphide in the crystalline state is not decomposed by hydrochloric acid, but the amorphous substance is slowly dissolved with evolution of sulphuretted hydrogen; hot nitric acid oxidises the amorphous sulphide, but not the crystalline substance; nitrohydrochloric acid oxidises it in both states, forming stannic oxide and sulphuric acid. When melted with litharge, stannic sulphide is decomposed, yielding metallic lead, sulphurous oxide and a yellow glass, or mixtures of both metals in the state of oxide and sulphide according to the proportions of the two substances.

Stannic sulphide combines with metallic sulphides forming a series of saline compounds called sulphostannates, in which it acts the part of an acid, and these salts correspond to the stannates, but contain sulphur in place of oxygen. The hydrogen salt H_2SnS_3 or $H_2S.SnS_2$ is a yellow precipitate formed on adding an

acid to the solution of an alkaline sulphostannate. The ammonium salt $2NH_4.SnS_3$ is soluble; the potassium salt K_2SnS_3 is a heavy dark brown oily liquid; the sodium salt forms crystals containing water $Na_2SnS_2 2H_2O$, and it combines with sodium sulphide, forming a colourless crystallisable salt resembling gypsum, the composition of which is represented by the formula $Na_2SNa_2SnS_3 12H_2O$. The corresponding barium, calcium and strontium salts are sparingly soluble in water. The compound of tin and sulphur, called sesquisulphide Sn_2S_3, intermediate between stannous sulphide and stannic sulphide, is probably a stannic sulphostannate $SnSnS_3$; it is a greyish yellow substance with metallic lustre, or a liver-coloured powder when obtained by digesting stannic sulphide with a saturated solution of sulphostannate.

Preparation.—Stannic sulphide may be prepared by heating a mixture of tin filings, sulphur, and ammonium chloride or mercuric chloride. So much heat is evolved by the combination of the tin and sulphur, that the sulphide would be decomposed unless this heat were absorbed by volatilisation of the ammonium chloride. There is, however, a chemical action between the tin and the ammonium chloride, according to the following equation:

$$2Sn + 4NH_4Cl = 2NH_4Cl.SnCl_2 + 2H + 2NH_3.$$

The ammonium chlorostannate thus formed is again decomposed by reaction with sulphur, yielding stannic sulphide and ammonium chlorostannate, according to the following equation:

$$2(2NH_4Cl.SnCl_2) + 2S = SnS_2 + 2NH_4Cl.SnCl_4 + 2NH_4Cl.$$

Stannous oxide, stannous sulphide, or stannous chloride may be substituted for the metallic tin in preparing stannic sulphide. The mixture is heated in a glass retort or flask until the excess of sulphur is driven off from the stannic sulphide.

Stannic sulphide is obtained in the amorphous form by passing sulphuretted hydrogen into a solution of stannic chloride.

Uses.—The crystalline variety of stannic sulphide is used under the name of mosaic gold for coating objects in imitation of bronze. Sometimes also it is used in place of the amalgam of tin and zinc, for coating the rubbers of electrical machines.

TITANIUM.

Symbol Ti. Atomic Weight 50.

This elementary substance was discovered in 1789 by Gregor as a constituent of a Cornish mineral called menaccanite, and in 1795 Klaproth discovered the same substance in rutile: in 1802 Vauquelin showed that anatase consisted essentially of a compound of this substance with oxygen, and in 1822 Wollaston ascertained the presence of a compound of titanium and nitrogen among the products of iron smelting furnaces.

Titanium does not occur naturally in the free state, but is most frequently met with in combination with oxygen either as rutile, anatase, and brookite, or combined with lime as perowskite, with ferrous oxide as ilmenite and several analogous minerals, among which are the various kinds of titaniferous iron ore. The compound of titanic oxide and lime also occurs combined with calcium silicate as sphene or titanite; titanium occurs likewise in a number of rare minerals containing cerium, yttrium, tantalum, and niobium; some iron ores contain titanium in small amount.

Titanium, as usually obtained by the reduction of the oxide, or by heating the double titanium and potassium fluoride with metallic potassium, is in the form of a dark greenish-coloured amorphous powder, but it may be obtained in prismatic crystals by heating sodium in the vapour of titanium chloride: heated in atmospheric air, in oxygen, or in chlorine, it burns with great brilliancy; it does not decompose water until the temperature is raised to 100°. Titanium is dissolved by hydrochloric acid, and it has a great disposition to combine with nitrogen at a high temperature.

There are at least two series of titanium compounds, in one of which that substance is quadrivalent, while in the other it is apparently trivalent, as in the oxides

TiO_2 and Ti_2O_3, or in the chlorides $TiCl_4$ and Ti_2Cl_6. There is probably another series of titanium compounds corresponding to an oxide having the formula TiO.

Titanium unites with aluminum, forming a yellowish-brown crystalline alloy: it is also found in some kinds of pig iron, and its presence in iron is said to be advantageous, but it is still doubtful whether the titanium in iron exists as an alloy, or merely disseminated through the mass.

Titanous oxide Ti_2O_3 is a black pulverulent substance obtained by heating titanic oxide to redness in contact with hydrogen. In this state it is not dissolved by nitric acid or hydrochloric acid, but sulphuric acid dissolves it, forming a violet-coloured solution, from which a crystalline deliquescent salt having the formula $Ti_2O_3 3SO_3$ may be obtained by evaporation over sulphuric acid.

The hydrated titanous oxide obtained by adding ammonia to a solution of titanous chloride is a dark brown substance, insoluble in water but soluble in acids, and apparently forming salts, though the sulphate is the only one that has been obtained in a solid state. Titanous hydrate gradually oxidises, turning black, blue, and eventually white, while hydrogen is evolved; the blue colour is probably due to the formation of a titanous titanate.

Titanic oxide TiO_2 is a reddish-coloured substance fusible only at a very high temperature, insoluble in water and all acids except strong sulphuric acid; as it occurs naturally it is crystalline, and crystals of it may be obtained by decomposing the vapour of titanic chloride by steam in a red-hot tube.

Titanic oxide forms saline compounds with basic oxides, the hydrate $2H_2O\ TiO_2$, or hydrogen salt, called titanic acid, and corresponding to stannic acid, being the representative of the compounds called titanates.

There is also another hydrate analogous to metastannic acid, which is called metatitanic acid, and there is a corresponding series of metatitanates.

Titanic acid is obtained by adding ammonia to solution of titanic chloride, as a white pulverulent substance which acquires a yellowish colour when heated, and becomes white again on cooling. At a high temperature it loses water, and is converted into titanic oxide, with vivid incandescence. Titanic acid is dissolved readily by hydrochloric, nitric, and sulphuric acids, even when they are dilute, and when the dilute solutions are boiled, metatitanic acid is deposited as a white powder, insoluble in all acids but strong sulphuric acid. Titanic acid is also converted into metatitanic acid by washing with hot water and by drying it at a high temperature.

The other saline compounds in which titanic oxide acts the part of an acid oxide present a general analogy with the stannates and silicates. The potassium salt K_2TiO_3 obtained by fusing titanic oxide with potassium carbonate is a yellowish fusible mass decomposable by water into an insoluble acid salt, and a soluble salt containing a larger proportion of basic oxide. The sodium salt is similar. Calcium titanate $CaTiO_3$ occurs naturally as perowskite, and in combination with calcium silicate as sphene or titanite $CaTiO_3\ Ca\ SiO_3$. Ferrous titanate Fe_2TiO_4 is a constituent of ilmenite and the varieties of that mineral comprised under the name of titaniferous iron ore.

Titanic oxide also presents the character of a feeble base, and it forms saline compounds with some acid oxides; the sulphate TiO_2SO_3 is formed when titanic oxide is dissolved in strong sulphuric acid; the solution gelatinises on cooling, and when part of the sulphuric acid is evaporated, a white powder is obtained, the composition of which corresponds with the above formula; it is soluble in hydrochloric acid, and when ignited gives off all the sulphuric acid. The nitrate obtained by dissolving titanic hydrate in nitric acid forms crystalline laminæ imperfectly soluble in water; the phosphate is formed on adding ammonium phosphate to a solution of titanic hydrate in hydrochloric acid, as a white gelatinous precipitate; and the oxalate is a curdy mass obtained on boiling the aqueous solution of a titanic salt with oxalic acid.

Titanic oxide does not dissolve in solution of caustic alkali; but it may be rendered soluble by fusion with acid potassium sulphate, and in this particular it differs from silica.

Titanous chloride, Ti_2Cl_6, presents the form of violet-coloured scales soluble in water; it is volatilisable, deliquescent, and readily oxidised.

Titanic chloride, $TiCl_4$, is a colourless volatile liquid; its specific gravity is 1·76 at 0°, and it boils at 135°; it is obtained by passing chlorine over an ignited mixture of titanic oxide and carbon; when exposed to the air it absorbs moisture and forms a crystalline hydrate, but is decomposed when mixed with a large proportion of water; it forms double salts with ammonium chloride, and combines with ammonia, cyanogen, hydrocyanic acid, phosphine, and sulphur tetrachloride. When heated in contact with hydrogen, it is converted into titanous chloride.

Titanic sulphide, TiS_2, which is the only known compound of titanium and sulphur, resembles the corresponding tin compound.

The nitrides TiN_2, Ti_3N_6, and Ti_5N_8 are violet or copper-coloured substances. The

compound of titanic cyanide, $TiCy_2$, with another nitride, Ti_3N_2, is sometimes found, in the form of copper-coloured crystals, among the products of iron-smelting furnaces, and it was for a long time supposed to be metallic titanium. The composition of this substance is represented by the formula $TiCy_2 3Ti_3N_2$. Its production is probably connected with the formation of potassium cyanide, which is frequently observed in iron furnaces.

Titanic fluoride, TiF_4, is a colourless volatile liquid; it combines with hydrofluoric acid and other fluorides, forming a series of crystalline salts called fluotitanates, which are isomorphous with the fluosilicates, fluostannates and fluozirconates.

TUNGSTEN.

Symbol W. Atomic Weight 184.

This elementary substance was first isolated by the brothers D'Elhujar in 1783, and shortly before both Scheele and Bergman had come to the conclusion that the mineral wolfram contained a peculiar metallic oxide combined with iron in an oxidised state. Tungsten occurs only in the oxidised state, either as wolframite, or combined with ferrous oxide and manganous oxide as wolfram, or with lime as scheelite, and with lead oxide as scheeletine.

As prepared by reduction of the oxide, tungsten is a steel-grey powder which acquires a metallic lustre by burnishing; the specific gravity is about 17·6; it melts only at a very high temperature. When heated in contact with atmospheric air in a pulverulent state, tungsten is oxidised and converted into tungstic oxide; but when heated in a compact state it undergoes no change; aqua regia, or nitric acid, converts it into tungstic acid, and by fusion with caustic or carbonated alkalies, or by boiling with solutions of those substances, it is converted into a soluble alkaline tungstate. Tungsten may be prepared from the oxide or nitride by heating either of them to redness in a stream of hydrogen, or by submitting a mixture of tungstic oxide and carbon to an intense heat in a crucible lined with charcoal.

Tungsten forms compounds in which it is respectively quadrivalent and sexivalent, as in the chlorides WCl_4 and WCl_6, or the oxides WO_2, WO_3. Neither of the oxides forms saline compounds with acid oxides, but tungstous oxide, WO_2, combines with soda, forming sodium tungstite Na_2O2WO_2, and tungstic oxide combines with bases to form the tungstates.

There is an intermediate series of compounds represented by the chloride W_2Cl_{10} and the oxide W_2O_5, which are probably compounds of tungstous chloride or tungstous oxide with tungstic chloride and tungstic oxide.

The bromides, fluorides, sulphides, and phosphides are represented by the formulæ WBr_4, W_2Br_{10}, WF_6, WS_2, WS_3, W_3P_4, W_2P. Tungsten has been alloyed with several other metals; it forms with steel an extraordinarily hard alloy, containing 9 to 10 per cent. of tungsten: wootz, or Indian steel, contains tungsten. The presence of tungsten in steel is said to increase its power of retaining magnetism.

Tungstic oxide WO_3 occurs naturally as wolframite or as wolframochre, accompanying other minerals containing tungsten. It is a yellow powder insoluble in water and in acids, but soluble in alkalies, and may be obtained in a crystallised condition. When heated the yellow colour changes to green without any chemical alteration, and on cooling the yellow colour returns. Reducing agents convert it into the brown tungstous oxide, and when heated to redness on charcoal it is reduced to the metallic state. Tungstic oxide combines with basic oxides, forming the salts called tungstates, and the hydrate WO_3H_2O or tungstic acid is obtained, as a yellow precipitate, when a hot solution of an alkaline tungstate is mixed with hydrochloric acid. Another hydrate $WO_2 2H_2O$ is formed, as a white gelatinous precipitate, when a cold dilute solution of alkaline tungstate is mixed with an acid, or when tungstic chloride is mixed with a large proportion of water. Tungstic acid is insoluble in water and in most acids, but there is a modification of it corresponding to metastannic acid and metatitanic acid, which is very soluble in water, forming a syrupy liquid of sour and bitter taste. It is obtained in form of a salt by boiling an ordinary alkaline tungstate with excess of tungstic hydrate.

The salts corresponding to tungstic acid and metatungstic acid are somewhat complex in character. The alkaline tungstates and magnesic tungstate only are soluble in water, whilst nearly all the metatungstates are soluble. The alkaline tungstates are obtained from wolfram by fusion with alkaline carbonates, the sodium salt, from which most of the other salts are prepared, being represented by the formula Na_2OWO_3.

Sodium tungstate has been used as a mordant in dyeing and in calico printing, and more particularly to render cotton fabrics uninflammable.

Metatungstic acid is said to be a delicate test for detecting organic bases when occurring in solution, excelling in that respect phosphomolybdic acid.

Tungstic chloride WCl_6 forms dark violet scales, which by sublimation can be obtained in needles having a metallic appearance. It may be prepared by heating tungsten or its sulphide in chlorine gas; also by passing chlorine over an ignited mixture of tungstic oxide and charcoal. It melts at 183° to a black liquid: its vapour density is 11·86. Heated in contact with air, tungstic chloride is converted into the red monoxychloride WCl_4O, and tungstic hydrate $WO_3\ 2H_2O$. Alkalies dissolve it with the formation of tungstates. Two compounds of tungstic chloride with tungstic oxide are known; the dioxychloride $WCl_6,\ 2WO_3$ is a yellow solid, volatilising at about 265°, which is formed when tungstic dioxide is heated in chlorine; the red monoxychloride $2WCl_6WO_3$ is produced by the action of heat on the dioxychloride.

MOLYBDENUM.

Symbol Mo. Atomic Weight 96.

The existence of this elementary substance as a peculiar constituent of the mineral molybdenite was first indicated in 1778 by Scheele, who established the distinction between that mineral and graphite, with which it had previously been confounded. The terms *μόλυβδος*, plumbago, were vaguely applied by Dioscorides and Pliny to litharge, galena, and other substances containing lead, and at a later period antimonous sulphide, graphite, and native manganese peroxide were regarded as being closely related, if not identical with molybdenite, until Pott proved, in 1740, that it did not contain lead. In 1781 Bergman suggested that the substance produced by oxidising molybdenite might be a metallic oxide, and in 1782 he announced that it had been reduced by Hjelm. In 1797 Klaproth showed that wulfenite was a lead molybdate.

Molybdenum occurs only in combination, either with sulphur as molybdenite, or in the oxidised state combined with lead oxide as wulfenite. It is a white and brittle metallic substance, with a specific gravity of 8·6. At the ordinary temperature it is unoxidisable in the air, but it burns when heated, forming a trioxide. Nitric acid oxidises it first to molybdic dioxide, then to the trioxide; sulphuric acid converts it into molybdic dioxide, then into the blue oxide, or molybdic molybdate $MoO_2,\ 4MO_3$.

Molybdenum may be prepared by reducing the oxides with hydrogen or by exposing them to a white heat in a crucible lined with charcoal. It forms compounds in which it is respectively bivalent, quadrivalent, and sexivalent; as in the oxides MoO, MoO_2, MoO_3, or the chlorides $MoCl_2$ and $MoCl_4$, and the fluoride MoF_6. Both molybdous oxide MoO and molybdic oxide MoO_2 combine with acid oxides forming salts, and molybdenum trioxide combines with basic oxides forming the molybdates.

Molybdenum unites with most metals, rendering them less fusible but more brittle.

The alloy of molybdenum and iron is sometimes formed in smelting copper ore, and constitutes the deposits known as 'bears' which are found in the furnaces.

Molybdous oxide MoO is black in ordinary daylight; it combines with acid oxides, forming molybdous salts, and is obtained in the hydrated state as a black precipitate by adding ammonia to the dark-coloured solution of molybdous chloride formed when one of the higher oxides is brought into contact with hydrochloric acid and zinc, or one of the metals which decompose water. The anhydrous oxide is obtained by drying the hydrate in a vacuum; it is insoluble in acids and oxidises when exposed to the air. The hydrate is dissolved by acids, forming molybdous salts, the solutions of which are black or purple and nearly opaque, except when largely diluted, when they have a greenish-brown colour; these salts have an astringent taste, and when exposed to the air they undergo oxidation.

Molybdic oxide MoO_2 has a reddish-brown colour, and combines with acid oxides forming molybdic salts; as obtained by reducing molybdic trioxide with hydrogen; it is insoluble in acids and in caustic alkalies, but is oxidised by ignition in contact with atmospheric air and by nitric acid. In the hydrated state it is obtained as a reddish-brown precipitate by adding ammonia to a solution of molybdic chloride or some other molybdic salt. The hydrate is sparingly soluble in water, and is dissolved by acids, forming dark red solutions of molybdic salts; it is insoluble in caustic alkalies, but dissolves in solutions of ammonium carbonate or potassium carbonate, and more readily in a solution of acid carbonate; on boiling these solutions molybdic oxide is precipitated of a yellowish colour.

Molybdenum trioxide MoO_3, or permolybdic oxide, occurs naturally as molybdic ochre, sometimes in rhombic prisms; as prepared artificially, it is white and porous, having a specific gravity of 3·49. It melts at a red heat, then sublimes in laminæ, but when heated out of contact with air it does not volatilise. Hydrogen, charcoal, and sodium, with the aid of heat, reduce it to the metallic state. It is very sparingly soluble in water. Molybdenum trioxide may be prepared by heating native molybdic sulphide in a current of air in an open glass tube, when the trioxide sublimes in a pure state.

Molybdenum trioxide forms with bases well-characterised neutral and acid salts called molybdates; the neutral salts may be represented by the formula of the ammonia salt $2NH_4\ MoO_4$. The neutral alkaline molybdates formed by digesting the trioxide with alkalies are very soluble in water; the other molybdates are insoluble and are obtained by precipitation. Lead molybdate $PbMoO_4$ occurs naturally as wulfenite.

With some acids molybdenum trioxide also forms compounds; permolybdic phosphate is a yellow insoluble salt, sometimes called phosphomolybdic acid; it is obtained by digesting the trioxide in aqueous phosphoric acid. A fine yellow precipitate of unascertained composition is produced by the addition of ammonic molybdate to a solution containing phosphoric acid, and this reaction is employed to detect phosphoric acid.

Molybdic sulphide MoS_2 occurs naturally as molybdenite in veins of iron and tin ores. It is of a lead-grey colour, with metallic lustre; sp. gr. about 4·4. It undergoes no change when heated out of contact with air; but in contact with air it is converted into molybdenum trioxide, with evolution of SO_2. At a red heat it decomposes water vapour. It is dissolved by aqua regia, forming molybdic acid and sulphuric acid; and is oxidised by nitric acid. It may be prepared artificially by heating molybdenum trioxide with sulphur.

Molybdenum forms two other sulphides, the trisulphide MoS_3 and the tetrasulphide MoS_4, both of which combine with basic sulphides, forming sulpho-salts—namely, the sulphomolybdates and the persulphomolybdates represented by the formulæ K_2SMoS_3 or K_2MoS_4 and K_2SMoS_4 or K_2MoS_5.

VANADIUM.

Symbol V. Atomic Weight 51·2.

This elementary substance was discovered in 1830 by Seftström as a constituent of the iron ore of Taberg in Sweden, and in a previous investigation of a lead ore from Zimapan in Mexico, Del Rio had detected it as a peculiar metal, to which he gave the name of erythronium. The chemical relations of vanadium were more fully studied by Berzelius, and in 1830 Wöhler showed that the Mexican mineral examined by Del Rio was lead vanadate. More recently, Roscoe has shown that the substance regarded by Berzelius as vanadium was really an oxide.

Vanadium occurs chiefly in the oxidised state and in combination with lead oxide as dechenite and descloizite; also combined with lead chloride as vanadinite; it has been also found in some iron ores and in the cupriferous sandstone of Cheshire.

As prepared from the chloride by the action of hydrogen at a red heat, vanadium is crystalline, and of a silver-white lustre; it does not change when in contact with the air at the ordinary temperature, or at 100°; but when ignited in contact with at-

mospheric air it gradually absorbs oxygen, becomes brown, possibly in consequence of the formation of the monoxide V_2O, and is eventually converted into the pentoxide V_2O_5; it combines directly with oxygen, chlorine, and nitrogen, forming respectively the pentoxide, tetrachloride, and vanadic mononitride. It is insoluble in either hot or cold hydrochloric acid, but soluble in sulphuric acid, nitric acid, and in hydrofluoric acid, with evolution of hydrogen.

Vanadium may be prepared in the pure state by reducing one of the vanadic chlorides in a stream of hydrogen.

In its compounds it is, according to Roscoe, analogous to arsenic and phosphorus, in being pentavalent, as in vanadic oxide V_2O_5, in sodium orthovanadate $3Na_2O.\ V_2O_5 = 2Na_3VO_4$, sodium pyrovanadate $2Na_2O.V_2O_5 = Na_4V_2O_7$, vanadic oxytrichloride $VOCl_3$, and it resembles nitrogen in its oxides, V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5.

The three chlorides VCl_2, VCl_3, and VCl_4 have been obtained, the first two from the decomposition of the tetrachloride, which is a reddish-brown liquid of 1·85 sp. gr. at 0°, produced when the metal or its nitride is heated in a current of chlorine. The oxychlorides and oxybromides are represented by the formulæ $VOCl_3$, $VOCl_2$, VOCl, V_2O_2Cl, and the tribromide by the formula VBr_3.

Vanadic pentoxide V_2O_5 is a reddish-yellow solid with an acid reaction, and requiring 1,000 parts of water to dissolve it. It is unalterable by heat. The stronger acids dissolve it, forming crystalline vanadic salts, but it also combines with basic oxides, and by fusion with alkaline carbonates it yields the saline compounds called vanadates.

It may be prepared from ammonic vanadate by heating that salt to a temperature below redness.

Vanadic anhydride forms compounds with bases much more readily than with acids. The vanadates resemble the phosphates in composition, but differ from them in being stable in a reverse order, the metavanadates being more stable and the orthovanadates being the less stable compounds.

The metavanadates, of which the composition may be represented by the formulæ of the ammonium salt NH_4VO_3, and the barium salt $Ba2VO_3$, are yellow, and some of them change into colourless isomeric compounds when heated.

Plumbic and argentic orthovanadates Pb_32VO_4, Ag_3VO_4, with the argentic pyrovanadates $Ag_4V_2O_9$, which may be taken as types of these compounds, are obtained by adding a soluble metallic salt such as argentic nitrate to the corresponding sodium vanadate.

Vanadic dioxide V_2O_2, which was regarded by Berzelius as vanadium, the trioxide V_2O_3, and the tetroxide V_2O_4, may all be prepared by reduction of the pentoxide; the dioxide prepared by reducing a solution of the pentoxide in sulphuric acid, after passing from blue to lavender, finally exists as a hypovanadous salt, which is remarkable for being equal to chlorine in its bleaching action.

The tetroxide forms insoluble salts with nearly all bases; it also dissolves in acids, giving blue solutions of a vanadous salt. These vanadites in the presence of water become green vanadites.

Vanadic pentasulphide can only be prepared in the wet way. It is obtained as a brown precipitate by adding hydrochloric acid to a solution of the pentoxide or alkaline vanadate in an alkaline sulphide. It is decomposed when heated out of contact with air, into sulphur and the tetrasulphide; heated in air it is oxidised to vanadic pentoxide and sulphurous anhydride.

With metallic sulphides it combines to form a class of sulphur salts—namely, the sulphovanadates.

There is also a tetrasulphide V_2S_4, analogous to the tetroxide, from which it is obtained by ignition in a stream of sulphuretted hydrogen. Vanadic tetrasulphide forms the sulphovanadites by combination with basic metallic sulphides.

NIOBIUM.

SYMBOL Nb. ATOMIC WEIGHT 94.

This elementary substance was discovered in 1801 by Hatchett in an American mineral called columbite, and hence it was termed columbium. In 1809 Wollaston pronounced it to be identical with the tantalum found by Ekeberg in Swedish tantalite, and this idea prevailed until 1846, when Rose showed that it was incorrect, and that the two metals were distinct. He found that the American mineral contained an acid metallic oxide which he named niobic oxide, and to the metal he gave the name niobium.

Niobium occurs in columbite as niobic oxide, combined with the ferrous oxide and manganous oxide; it is also associated with yttrium, uranium, iron, etc., in a number of Siberian minerals, and in a variety of pitchblende from Satersdälen in Norway.

The metal is obtained by heating the fluoride with metallic sodium in a covered iron crucible, and washing out the soluble part of the fused mass with water. Thus obtained, it is a black powder with a sp. gr. 6·27–6·67, which oxidises with incandescence when strongly heated in the air. When strongly heated in chlorine gas it yields niobic chloride; it dissolves in boiling dilute hydrochloric acid and in hot hydrofluoric acid, with evolution of hydrogen, but is not dissolved by nitric acid, and only slowly by nitrohydrochloric acid.

Niobium is pentavalent in its compounds. The chloride $NbCl_5$ is a volatile, fusible substance, obtained by the action of chlorine at a red heat upon the corresponding oxide mixed with charcoal; a corresponding fluoride is also known, as well as an oxychloride, and an oxyfluoride $NbOCl_3$ and $NbOF_3$.

Two bromides are also known, a nitride, a sulphide, and a number of double fluorides which have been investigated by De Marignac.

Elaborate investigations of the natural niobates have also been recently published by Rammelsberg.

TANTALUM.

SYMBOL Ta. ATOMIC WEIGHT 182.

This elementary substance was discovered in 1802 by Ekeberg, as a constituent of the Swedish minerals tantalite and yttrotantalite.

It occurs only in the oxidised state, combined with yttria, ferrous oxide, and other basic oxides; it is often associated with niobium in the various natural niobates and tantalates which Rammelsberg has shown to be represented by the formulæ RNb_2O, $R_2Nb_2O_7$, and $R_3Nb_2O_8$, corresponding to the phosphates and arsenates. Tantalum also occurs as a constituent of some varieties of wolfram.

Tantalum, as obtained by heating potassium fluotantalate with metallic sodium in a covered iron crucible, is a black powder which conducts electricity well, and after ignition in hydrogen has a specific gravity 10·78. When heated in the air, it burns with a bright light, and is oxidised. It dissolves readily in hydrofluoric acid, with evolution of hydrogen, but is not attacked by other acids.

Tantalum forms two series of compounds corresponding to the dioxide TaO_2 and to tantalic oxide Ta_2O_5, which latter oxide unites with bases and forms salts. In most of its compounds it is pentavalent.

By passing chlorine over tantalic oxide heated to redness with charcoal, a volatile pentachloride is formed ($TaCl_5$), and a corresponding bromide is known less well.

A similar fluoride is known, a nitride, and a sulphide.

Both tantalum and niobium appear to resemble vanadium in being more intimately related to the phosphorus group than to silicon.

THALLIUM.

SYMBOL Tl. ATOMIC WEIGHT 203·6.

This metal was discovered by Crookes in 1862, during the spectroscopic examination of a seleniferous deposit from a sulphuric acid works. The green line which it exhibits in the spectrum suggested to him the name which he gave to the metal.

Soon after Crookes had announced his discovery, Lamy obtained it more abundantly from a like source.

Thallium is but sparingly distributed in nature. Nordenskiöld found from 16 to 19 per cent. thallium in a selenide of copper and silver from Skrikerum in Sweden, to which he gave the name crookesite. Hitherto the metal has been principally obtained from the Spanish, Belgian, and Bolivian pyrites. It is a soft, heavy, diamagnetic metal, of a lustre resembling that of cadmium, but tarnishing on exposure.

Regnault has assigned to it a specific heat of 0·03355, while Lamy found 0·0325. It is a crystalline metal, which crackles like tin when bent; but from its soft nature it admits of hammering out into foil or drawing into wire, although its tenacity is small. According to Crookes it melts at 293·9° C. (290° C. Lamy), undergoes atmospheric oxidation, and if heated to 315° C. in oxygen, takes fire and burns with a green light. The metal is volatile, and boils below a white heat; it may be distilled in a current of hydrogen.

It combines directly with chlorine, bromine, iodine, sulphur, and phosphorus; and most of the acids attack it readily with evolution of hydrogen; the chloride being insoluble, hydrochloric acid does not exercise a powerful action upon the metal.

The thalliferous dust deposited in the flues of sulphuric acid works is the best source of the metal, which may be obtained by extracting the dust with dilute sulphuric acid, and precipitating the solution with hydrochloric acid. By suspending the impure thallic chloride thus obtained in a solution of carbonate of sodium, and passing a current of chlorine through the mixture, insoluble thallium peroxide is obtained, which after washing may be resolved into sulphate by suspending it in water and submitting it to the action of sulphurous anhydride. On evaporation the sulphate is obtained in a crystalline form. From its solution the metal may be precipitated by the action of metallic zinc or by electrolysis. It can be obtained in the dense metallic state by fusion out of contact with oxygen, as secured by covering it with potassic cyanide, etc.

Thallium forms two series of compounds corresponding to the oxides Tl_2O and Tl_2O_3. Thallous oxide Tl_2O is a very soluble substance. Its aqueous caustic solution absorbs carbonic anhydride readily from the air. By evaporation in vacuo the hydrate TlHO is obtained in crystals. Like silver compounds this gradually blackens by contact with the air, and fuses at 315° C. into a brown liquid. A solution of thallous oxide precipitates many metals as oxides from their solutions.

Thallic oxide Tl_2O_3 is formed during the electrolysis of thallous sulphate as a brown powder at the positive electrode. It may also be obtained by the action of hydric peroxide on the metal, or by the action of chlorine upon the chloride held in suspension in a solution of sodic carbonate. It is also formed by the action of ozone or peroxide of hydrogen upon paper impregnated with a thallous salt; hence this paper is really no absolute test for ozone, since hydric peroxide is known to behave like it.

Thallous chloride TlCl, molecular weight = 239·1, is a yellowish-white salt, sparingly soluble in water or ammonia. With ferric chloride it furnishes a double salt, $6TlCl, Fe_2Cl_6$, of a cinnabar-red colour, and crystallising in prisms. Water decomposes this compound into the respective chlorides. It also forms double salts with the chlorides of gold and platinum. Lamy has described three other chlorides of the composition Tl_2Cl_3, $TlCl_2$, and $TlCl_3$. Thallous iodide and bromide are yellow and but sparingly soluble. There are also a number of double chlorides, iodides, and bromides, which may be illustrated by the following examples: $3KCl,TlCl_3,2H_2O$; $3KBr\,2TlBr_3,3H_2O$; $3KI\,2TlI_3,3H_2O$, etc. Besides the normal salt there is also known an acid sulphate.

The nitrate $TlNO_3$ crystallises in anhydrous prismatic needles, which melt easily, and are insoluble in alcohol. It is obtained by dissolving the metal in nitric acid, and is isomorphous with the nitrates of potassium, sodium, etc. The carbonate $TlCO_3$ is also crystalline, as is the perchlorate $TlClO_4$ and the various phosphates.

Thallium may be easily alloyed with most of the metals, and several of these alloys have been studied by Carstanjen. Excepting the compound with tin, they all tarnish in the air, and all are more or less attacked by dilute sulphuric acid, with the evolution of hydrogen.

CERIUM.

Symbol Ce. Atomic Weight 138.

Cerium was discovered in 1803 by Klaproth and by Hisinger and Berzelius, who obtained it as oxide from cerite. It is a rare metal which has been found in but few minerals. It occurs in cerite, a hydrated basic ceric silicate, and also in churchite, which is a hydrous phosphate of cerium.

In cerite it is accompanied by lanthanum and didymium. As extracted from its chloride, it is a dark red or chocolate-coloured powder, assuming a metallic lustre on friction; it is infusible, and does not conduct electricity well.

Wöhler has given a method for extracting it from the oxide, by fusing it with mixed potassium and ammonium chlorides; on reduction of the fuse by metallic sodium at a high temperature metallic cerium is obtained.

Cerium oxalate CeC_2O_4, $3H_2O$ is one of the best known salts; it furnishes the oxide on ignition.

Two oxides are known; cerous oxide Ce_2O_3, and ceric oxide CeO_2, a body which is obtained in colourless transparent crystals with a density of 6·94. The cerous-potassic sulphate and cerous chloride, $2CeCl_3$, $9H_2O$, which forms colourless crystals, are both well-defined salts.

Marignac has obtained the sulphate $Ce(SO_4)_3 3H_2O$, and a number of other combinations are also known.

Ceric sulphate crystallises in a yellow indistinct form, $Ce(SO_4)_2 4Aq$.

DIDYMIUM.

Symbol Di. Atomic Weight 144·75.

This metal was discovered by Mosander in 1841, and its compounds have since been studied by him, also by Watts, Marignac, Hermann, Bunsen, and others.

It occurs associated with cerium and lanthanum in cerite, allanite, orthite, and allied minerals, but not in the free state; in fact, it is scarcely known in the metallic form.

It is said that the metal may be prepared by heating the chloride strongly with potassium, and washing out the soluble chlorides by water. It is thus obtained partly as a grey powder and partly in globules. The powder decomposes water at normal temperatures, and the metal in any form dissolves easily in dilute acids with evolution of hydrogen.

But few of its compounds are known. One oxide (Di_2O_3) is known, but it is probable that others exist, notably a peroxide.

The oxide (Di_2O_3) is obtained in the anhydrous state by ignition of the nitrate or the hydrate in a covered crucible; the anhydrous oxide becomes hydrated on immersion in water, dissolves easily in acids, and expels ammonia from solution of its salts when boiled with them.

Didymium gives a white oxalate, and forms double sulphates of a rose-red colour with potassium, sodium, and ammonium.

Chloride of didymium forms rose-coloured crystals of the composition $DiCl_3$, $4H_2O$. When a solution of it is evaporated, hydrochloric acid is evolved, and an oxide is left behind, thus behaving similarly to the chloride of magnesium.

Most of the salts of didymium are pink or violet-coloured, and are not precipitable by sulphide of ammonia; they possess also spectroscopic properties which are characteristic.

LANTHANUM.

Symbol La. Atomic Weight 139.

This metal was discovered by Mosander in 1841, and occurs along with didymium and cerium in cerite, and along with didymium in lanthanite as carbonate.

It forms two oxides, but the peroxide requires more precise study. The protoxide La_2O_3 is a buff-coloured substance obtained by ignition of the hydrate, carbonate, or oxalate, first in contact with the air, and afterwards in the reducing gases of the flame.

The peroxide dissolves in acids with evolution of oxygen.

Lanthanum forms colourless, astringent salts whose solutions give white precipitates with the soluble oxalates.

Sulphide of lanthanum is obtained by igniting the metal in the vapour of carbon disulphide; it is a yellow powder.

The chloride $LaCl_3$ is obtained in the anhydrous state by igniting the oxide in hydrochloric acid gas, or by dissolving the oxide in the acid, etc.

A hydrated chloride $LaCl_3 2H_2O$ which is crystalline and some other combinations are also known, such as the sulphate $La_2(SO_4)_3 9H_2O$ and the double salt $LaK_3(SO_4)_3$.

INDIUM.

Symbol In. Atomic Weight 113·4.

This metal was discovered in 1863 by Reich and Richter in the zinc blende of Freiberg, by means of its peculiar spectrum, which consists of two bright lines in the blue and indigo, one very bright, and the other fainter. It has been since found by Böttger in the flue-dust of the zinc furnaces of the Julius works at Goslar in the Hartz; by Winkler in the black blende (christophite) of Saxony, and by others in wolfram and steatite.

It has also been detected in certain zinc blendes from New Hampshire (U.S.) by H. B. Cornwall. Bayer suggested a process for the extraction of indium, which is as follows. Freiberg zinc is heated with a quantity of hydrochloric acid insufficient to entirely dissolve it, when, in the course of several days, the indium is precipitated upon the surface of the residual metal. The metallic mud is isolated, heated with a little dilute sulphuric acid to dissolve any oxychloride of zinc that may be present, and then thoroughly washed with hot water. The product is then heated with nitric acid, sulphuric acid added and the mixture evaporated to dryness; tin and lead are thus separated as oxide and sulphate. The residue is extracted with water at 100°C. and the solution after filtration precipitated by excess of ammonia, thus throwing down the indium and iron, and leaving copper, zinc, and cadmium in solution. The precipitate is washed. dissolved in the minimum amount of hydrochloric acid, and sodic-hydric sulphite added in excess. On boiling, the indium is obtained as sulphite, and by re-solution in sulphurous acid and re-precipitation by boiling the salt is obtained pure, of the composition $2In_2O_3\ SO_2 8H_2O$. This substance, treated with other acids, furnishes the various salts of indium. There are several other processes for extracting the metal from its ores.

The metal may be obtained from its oxide by reduction with hydrogen or sodium, or it may be precipitated from its solution by zinc and fused with potassic cyanide, giving a button of the metal.

Indium is a silver-white, soft, ductile, compact metal, destitute of crystalline structure, and having a sp. gr. 7·421 and a melting point of 176°. At higher temperatures suboxide is formed, if melted in the air. At a strong red heat the metal burns in air with a violet flame, and forms the same yellow oxide. In dilute sulphuric or hydrochloric acid it dissolves slowly, giving off hydrogen; nitric acid oxidises it. The chloride In_2Cl_6 is formed by heating the metal in chlorine, when it burns with a greenish light and the chloride sublimes in white laminæ; it forms double chlorides with those of the alkali metals. The bromide $In_2\ Br_6$ and Iodide $In_2\ I_6$ are both crystalline bodies, which may be prepared by heating the metal with bromine or iodine in an atmosphere of carbonic anhydride. Several oxides are known.

The yellow oxide In_2O_3 may be obtained by igniting the hydrate which is thrown down from the solutions of indium by ammonia, $In_2H_6O_6$. Indic oxide (In_2O_3) is readily soluble in acids and furnishes three other oxides by ignition in hydrogen; at 180°C. the green substance In_7O_9 is produced; at 220° C. the grey oxide In_4O_5 is formed; and at 300° C. a black compound, perhaps InO. These substances, however, have not been well examined. By fusing metallic indium with sulphur, indic sulphide In_2S_3 is obtained in shining scales resembling mosaic gold (Winkler). From a neutral or acetic acid solution of indium sulphuretted hydrogen precipitates yellow sulphide which dries to a brown colour and is decomposed by acids.

Indic sulphate is known, as also is the nitrate $In_2\ (NO_3)_6,\ 9H_2O$ as a crystalline substance which loses $6H_2O$ at 100°C.

The carbonate is a white gelatinous body as obtained by precipitation, it is soluble in ammonic carbonate, and is reprecipitated on boiling.

Neither the metal nor its salts are used in the arts.

Closely associated in many respects with indium is the new metal GALLIUM (symbol Ga; atomic weight 68) recently discovered by Lecoq de Boisbandrau in zinc blende from the mine of Pierrefitte. Gallium gives an oxide Ga_2O_3, and a chloride $GaCl_3$, and forms also an ammonium alum.

The specific gravity of the metal is 5·9 and its melting point 30·1°.

ZIRCONIUM.

SYMBOL Zr. ATOMIC WEIGHT 89·6.

The oxide of this element was first obtained from zircon, and was recognised as a peculiar body by Klaproth in 1789.

It is found as oxide in eudialyte, polymignite, œrstedite, fergusonite, and catapleiite. The zircon, like the hyacinth, is a silicate of the composition ZrO_2SiO_2, and is found in the Radau valley near Harzburg.

Zirconium is generally regarded as a tetratomic element, and may be obtained like silicium in three states—amorphous, crystalline, and graphitoïdal. Indeed, in its properties and compounds it ranges between silicium on the one hand and aluminum on the other hand.

Berzelius was the first (in 1824) to obtain the metal in its amorphous form; this he did by heating together potassio-zirconic fluoride $2KF,ZrF_4$ with metallic potassium.

Troost prepared it by passing the vapour of zirconic chloride over melted sodium at a red heat, or by heating the sodio-zirconic chloride with either metallic sodium or magnesium in a crucible.

The amorphous metal passes under the burnisher into a lustrous, graphitic-looking mass, which conducts an electric current but feebly. Heated in the air it takes fire below redness, and burns with a bright light, forming zirconia. It is attacked very little by acids, even by hydrochloric acid; but hydrofluoric acid dissolves it with evolution of hydrogen.

The crystalline variety is prepared by heating a mixture of 1 part potassio-zirconic fluoride with 1½ parts of aluminum in a plumbago crucible, to a temperature equal to that of melted iron. From the product the residual aluminum is dissolved out by hydrochloric acid, leaving nearly pure zirconium behind. Thus obtained, it resembles antimony in appearance, and has a specific gravity 4·15. It is very infusible, and burns only in the oxyhydrogen flame.

Fused caustic potash oxidises it, with evolution of hydrogen; nitrohydrochloric acid dissolves it when hot, with ease; but other acids act feebly on it.

Graphitoïdal zirconium is formed under conditions less well determined. Troost, in attempting to decompose zirconate of sodium with iron, obtained light scales of it, having a steel-grey colour.

Zirconium is closely allied to titanium. It forms but one oxide, ZrO_2; a tetrachloride $ZrCl_4$, and a corresponding tetrafluoride; also a bromide, nitride, and a number of fluozirconates, or double fluorides of zirconium and other metals.

Oxide of zirconium ZrO_2 is prepared by fusing a mixture of finely powdered zircon with caustic soda or potash, and saturating with hydrochloric acid; the mixture is evaporated nearly to dryness, and the zirconic chloride dissolved by water, leaving the silica behind. From the solution the zirconium is precipitated as thiosulphate (hyposulphite), and this on ignition gives pure zirconia.

Thus prepared, it is insoluble in acids, excepting concentrated sulphuric acid.

The hydrated oxide is a gelatinous white precipitate, insoluble in caustic alkalies.

ZIRCONIC CHLORIDE $ZrCl_4$ crystallises in needles which are soluble both in water and alcohol; when exposed to the air they lose water and hydrochloric acid and give a soluble oxychloride ($ZrCl_4$, ZrO_2, $18H_2O$).

It may be prepared by heating the metal in chlorine gas, or by heating the oxide with charcoal in a current of dry chlorine. It is a volatile body, with a vapour density of 8·15 (Deville and Troost).

GLUCINUM.

Symbol G or Be. Atomic Weight 9·4.

The oxide of this metal, sometimes termed berylium, was discovered by Vauquelin in 1798; but the metal itself was first obtained by Wöhler and Bussy in 1828, by fusing the chloride with potassium. It may be extracted from the emerald or the beryl, which consists in great measure of silicate of aluminum and glucinum $3GO$, Al_2O_3, $6SiO_2$. It occurs also as a silicate in the mineral phenacite; with other silicates it is found in various other minerals, and as aluminate it occurs in chrysoberyl or cymophane.

Glucinum is a white, malleable metal, more fusible than silver, and combines readily with chlorine, iodine, and silicon. It is easily dissolved by dilute hydrochloric or sulphuric acid, but is not vigorously attacked even by strong nitric acid. In potash it dissolves with the evolution of hydrogen.

Debray regards glucinum as monatomic in character; but there appears to be some doubt regarding its atomicity.

Beyond the method given above for the preparation of the metal, the following one by Debray may be adopted for extracting it in a compact state. Chloride of glucinum is first introduced into a combustion tube, and the air then expelled by a current of hydrogen, after which metallic sodium is introduced and heat applied. The chloride of glucinum volatilises, and thus coming into contact with the melted sodium, it is reduced, forming a black mass with the salt, from which the globules of metal are obtained on treating the fuse with water. Thus obtained, it has a specific gravity 2·1, and may be forged and rolled into sheets like gold.

Only one oxide of the metal is known, and, as yet, the formula has not been thoroughly established; by some it is regarded as a protoxide (GO) and by others as a sesquioxide (G_2O_3). It may be obtained from the beryl, which contains 10·6 per cent. of this substance. The silicon is first of all removed as silicic fluoride by heating the mineral with fluospar and sulphuric acid; the residue is ignited to redness, dissolved in dilute sulphuric acid, and sulphate of ammonium added. By a process of crystallisation the aluminum is removed as alum, and any which remains behind is deposited as basic sulphate on digesting the mother liquor with metallic zinc. The zinc has then to be removed by addition of sodic acetate, and precipitation by sulphuretted hydrogen, after which glucina is obtained on adding excess of ammonia.

Several sulphates of the metal are known, the principal one being GSO_4, $4H_2O$, which crystallises in octohedra.

A great number of phosphates are also known. Heated in bromine vapour, the metal takes fire, and forms a bromide GBr_2, which sublimes in colourless prismatic crystals; it is a fusible volatile body.

Chloride of glucinum GCl_2 is formed by heating the metal in chlorine gas or hydrochloric acid. The anhydrous salt is obtained by passing chlorine over an ignited mixture of glucina and charcoal; the hydrated salt crystallises with one molecule of water, GCl_2, H_2O.

From many of its characters it appears to be a member of that group of metals characterised by aluminum.

Very little is known about the alloys of glucinum. According to Stromeyer, by heating the oxide to whiteness, with iron and charcoal, an alloy with iron is obtained. H. Dairy also obtained an alloy with iron, by decomposing glucina in an atmosphere of hydrogen, by a powerful voltaic current, having the negative pole of the battery formed of an iron wire which is fused by the current.

THORIUM.

Symbol Th. Atomic Weight 231·5.

This metal was discovered in 1829 by Berzelius, in a rare black mineral—thorite, which occurs in a syenitic rock in Norway. Since then it has been found in pyrochlore by Wöhler, in monazite by Karsten, in euxenite, gadolinite, orthite, etc.

As prepared from its chloride by heating with potassium or sodium it is a grey metallic powder of sp. gr. 7·6 to 7·8, closely resembling zirconium; it burns in the air with brilliancy and forms oxide.

Thoria (sp. gr. 9·402) is probably a dioxide, which is precipitated as a hydrate from the sulphate or chloride by ammonia, and this on ignition gives the anhydrous oxide (ThO_2) which is insoluble in acids, excepting strong sulphuric.

Thorium chloride $ThCl_4$ is prepared by heating an intimate mixture of thoria and charcoal in dry chlorine, when the salt, which is not very volatile, sublimes as a white crystalline mass.

By dissolving the hydrated oxide in hydrochloric acid, and concentrating the solution, the chloride is obtained as a deliquescent crystalline saline mass.

Ammonio-thoric chloride $4NH_4Cl,ThCl_4, 4H_2O$, is known, and also the corresponding potassic salt.

Fluoride of thorium has the composition ThF_4, while the hydrated fluoride is $ThF_4, 2H_2O$; there are known also a bromide and an iodide, an acetate, phosphide, sulphide, and a number of other compounds.

Thoric sulphate is deposited from its boiling solutions, and is redissolved on cooling.

The oxalate of thorium is white and insoluble.

YTTRIUM.

Symbol Y. Atomic Weight 92.

Gadolin in 1794 obtained from the ytterite or gadolinite of Ytterby in Sweden, a peculiar oxide resembling lime and alumina. In 1797 Ekeberg confirmed these results and named the earth yttria.

A number of chemists studied this substance and others accompanying it, and in 1843 Mosander, after a careful study of crude yttria, concluded that it contained three earths of different basicity; to the more abundant of these he gave the name yttria, and the others he named erbia and terbia. It is doubtful, however, whether terbia exists.

This metal, which belongs to the class known as earth metals, exists only in a few rare minerals.

Metallic yttrium is obtained by igniting its chloride with metallic potassium, and as thus prepared it is a blackish-grey powder, which acquires some lustre under the burnisher. Yttrium as thus obtained by Berzelius was, however, contaminated by erbium. It is of tritomic character, and forms only one series of compounds.

The oxide $Y_2O_3 = 232$ occurs naturally in gadolinite and in yttrotantalite. It is a white earthy powder of sp. gr. 4·842, insoluble in caustic alkalies, but dissolved by their carbonates. It may be obtained by ignition of the oxalate, and as thus prepared it differs from erbia, by yielding a spectrum without bright bands.

The chloride is a non-volatile salt obtained by heating the metal in a current of chlorine; the bromide is obtained by dissolving the oxide in hydrobromic acid; so, also, the iodide may be prepared in a corresponding way by using hydriodic acid.

Besides a selenide and a sulphide, which are known, there exists also a basic nitrate $Y(NO_3)_3Y_2O_3, 3H_2O$ which crystallises in needles.

The sulphate $3Y_2(SO_4)_3 8H_2O$ forms also well-defined crystals.

ERBIUM.

Symbol Eb. Atomic Weight 168·9.

Very little, indeed, is known about this metal or its compounds. It was discovered by Mosander in 1843, and is found as oxide associated with the oxide of yttrium in gadolinite. Erbia is a weaker base than yttria, and, as obtained by ignition of the precipitated hydrate, it has a deep yellow colour with a formula Eb_2O_3, and a doubtful molecular weight of 385·8. Its salts have a rose-red colour and astringent taste.

URANIUM.

SYMBOL U. ATOMIC WEIGHT 240.

History.—Uranium was discovered by Klaproth in 1786, in the mineral named pechblende or pitchblende, which had hitherto been regarded as a zinc ore. He assigned to the new metal the name of uranium, in honour of Herschel, who about the same time discovered the planet of that name.

Occurrence.—Uranium is a metal whose compounds are sparingly distributed in nature; the principal ore is pitchblende, a brownish-black mineral which is essentially uranoso-uranic oxide $UO_2.2UO_3$, of which it generally contains from 40 to 90 per cent. With this green oxide there are associated varying quantities of copper, lead, iron, arsenic, and sometimes nickel and cobalt.

Pitchblende is found in veins with lead and silver ores in Saxony, and with tin in Cornwall.

Uranite, a mineral of a micaceous character, and rarely met with, occurs in France, and is also found in a beautiful form near Redruth in Cornwall. It consists of a hydrated calcic diuranic diphosphate $Ca''2(U_2O_2)\ ''2PO_4,\ 8H_2O$.

Chalcolite is a corresponding mineral in which the calcium is replaced by copper.

Samarskite and uranotantalite, which contain oxide of uranium, together with yttria and niobic acid, are forms of minerals which are met with here and there; so also johannite (sulphate of uranium); zippeite (sulphate of uranium sesquioxide), and uranochre (an impure yellow oxide).

Beyond these a number of arsenites are found in the White Hart mine in Saxony, and according to Winkler contain from 50 to 63 per cent. of uranium oxide. His analyses lead to the following formulæ:—

		Specific gravity.
Trögenite . . .	$3UO_3.\ As_2O_5 + 12H_2O$	3·23
Walpurgite . .	$5BiO_2.\ As_2O_5 + 3UO_3.\ A_2O_5 + 10H_2O$	5·64
Zeunerite . . .	$CuO.\ 2UO_3.\ As_2O_5 + 8H_2O$	3·53
Uranospinite . .	$CaO.\ 2UO_3.\ As_2O_5 + 8H_2O$	3·45
Uranosphærite . .	$Bi_2O_3.\ UO_3 + H_2O$	6·36

Characters.—Uranium when in the metallic state constitutes a black coherent powder or is of a steel-white colour, according to the state of aggregation. Under ordinary atmospheric conditions it does not oxidise, but it burns brilliantly when heated in contact with the air. It combines with chlorine and sulphur with considerable violence, and is dissolved by sulphuric and hydrochloric acids with evolution of hydrogen. Chemically, it is allied in many respects to iron and manganese; but it possesses some characters which are not common to them. Thus it has a high specific gravity (18·4) and forms a volatile chloride (UCl_4); uranic oxide does not form salts similar to ferric chloride, and, while it is less easily reducible than iron, its oxides are weak bases compared to the oxides of iron. From these and other considerations Mendelejeff doubles the atomic weight ordinarily assigned to uranium, and makes it 240, regarding it as a hexad analogous to chromium.

Uranium forms three oxides—uranous or protoxide UO_2; uranoso-uranic oxide $UO_2.2UO_3$; and uranic oxide UO_3.

Peligot further admits the existence of two other combinations of the metal with oxygen.

Uranium is used for enamel painting and glass staining; the dioxide gives a fine black colour, not unlikely by absorbing oxygen and becoming black oxide. The sesquioxide gives a fine yellow colour.

Preparation.—The isolation of metallic uranium is due to Peligot, who showed that the substance originally regarded as such was uranous oxide.

The following method, which is the device of Valenciennes, is described by Peligot:—

A mixture, consisting of 75 grms. uranous chloride, 150 grms. potassic chloride,

and 50 grms. of metallic sodium cut into small pieces, is covered by potassic chloride in a crucible, which is enclosed in a second one, and the space between the two is packed with charcoal. The mixture is first exposed to a red heat, when the reaction occurs; after which the fire is strongly urged so as to melt the metal without volatilising the flux. The metal may be obtained by afterwards dissolving out the flux. To ensure success it is essential to carefully exclude all moisture; otherwise the chloride of uranium is converted into irreducible uranic oxide. As thus obtained, the specific gravity of the metal is 18·33.

To extract the metal from pitchblende, this mineral is heated to redness, and pulverised by throwing it whilst hot into water. The powder so obtained is washed with dilute hydrochloric acid, heated with charcoal, and then digested in stronger acid. In this way most of the iron, arsenic, and sulphur is removed together with the earthy matters. The washed product is roasted, then treated with nitric acid, and the resulting solution evaporated nearly to dryness to expel the acid. Water is then added, ferric arsenate is thrown down, and on passing sulphuretted hydrogen through the clear solution, copper, lead, and arsenic are precipitated as sulphides. After this treatment the solution is evaporated till crystals of uranic nitrate begin to form. The nitrate is next decomposed at a red heat, giving the oxide (U_3O_8), which is mixed with charcoal, and heated in a current of dry chlorine; carbonic oxide and carbonic anhydride are given off, and uranous chloride sublimes. On now heating this chloride with metallic potassium, intense heat is evolved, potassic chloride is formed, and metallic uranium results.

To obtain the metal in fused globules it is best to place layers of sodium, potassic chloride, and mixed potassic and uranous chlorides in a porcelain crucible enclosed in an earthen one lined with charcoal; on heating in a blast furnace the fused metal is obtained.

Compounds.—Uranium forms two chlorides, UCl_3 and UCl_4, and an oxychloride UO_2Cl_2.

The tetrachloride (UCl_4) is prepared as above described, and is a volatile deliquescent salt, which crystallises in dark green octahedra of a metallic lustre.

Uranous chloride is decomposed by boiling water; it is also decomposed by dry hydrogen, giving the sub-salt UCl_3, which is a crystalline body of dark brown colour, forming with water a purple solution. Ammonia precipitates from this latter a brown suboxide, which speedily absorbs oxygen on exposure to the air.

The oxychloride was made by Peligot, and is formed by the passage of chlorine over uranous oxide; it is a deliquescent substance, giving a yellow aqueous solution, and forming double salts. Thus, with potassic chloride, it gives $2KCl,UO_2Cl_2$, $2H_2O$ in rhombic plates of a greenish-yellow colour.

Uranium also forms bromides, corresponding apparently to the chlorides.

Uranic nitrate, like most of the salts, is yellow, and forms striated prisms of the composition expressed by the formula $UO_2''2NO_3$, $6H_2O$.

Uranium has a capacity for forming double salts; thus besides the double chloride above alluded to there is known a uranic potassic sulphate $K_2(UO_2)''2SO_4$, $2H_2O$.

When the salts of uranic oxide (UO_3) are heated with alkalies, the oxide is not obtained, but a yellow precipitate, which in the case of potassic hydrate has the formula $K_2O,2UO_3,3H_2O$, that is, uranate of potassium.

The commercial yellow oxide, or uranium yellow, is a hydrate retaining about 2 per cent. of ammonia; on heating, water and ammonia are liberated and the uranic oxide is converted into the black or green oxide.

Thallous oxide gives with uranium solutions a yellow precipitate of thallium uranate, analogous to the potassic salt described above. Normal uranic sulphate $(UO_2)''SO_4$ crystallises in yellow non-fluorescent crystals. When its solution in concentrated sulphuric acid is evaporated in an open dish at 200°, an acid sulphate $H_2(UO_2)\,2SO_4$ forms.

Uranic nitrate, heated with solution of tetrethylammonium hydroxide, gives a yellow precipitate of tetrethylammonium uranate $4C_2H_5.NO{\cdot}UO_3 + 3H_2O$.

Roscoe has recently studied the pentachloride of uranium UCl_5 which is obtained along with the tetrachloride or uranous chloride (UCl_4), by passing dry chlorine over a moderately heated mixture of any oxide of uranium, or the oxychloride and charcoal.

Uranic oxide forms no chloride, bromide, or iodide, nor are there normal uranic oxysalts; all the uranic salts contain the group UO_2 or uranyl, which plays the part of a bivalent radicle—for instance, in the following compounds:

Uranyl oxide, or uranic oxide $(UO_2)O$
Uranyl chloride, or uranic oxychloride $(UO_2)Cl_2$
Uranyl nitrate, or uranic nitrate $(UO_2)\,2NO_3$
Uranyl sulphate, or uranic sulphate $(UO_2)\,(SO_4)$.

URANOUS OXIDE.

FORMULA UO_2. MOLECULAR WEIGHT 272.

This oxide may be obtained in several ways, as by ignition of the oxalate in a closed crucible, or the potassio-uranic chloride in hydrogen. The anhydrous oxide is not attacked by dilute acids.

The hydrated oxide is produced by adding ammonia to a solution of uranous chloride UCl_4 and this reddish-brown precipitate is readily soluble in acids.

This oxide forms green salts of a crystallisable nature, exhibiting a tendency to absorb oxygen. On igniting the protoxide to redness, and suddenly cooling it, the black oxide U_2O_5 is obtained; it is also obtained by ignition of the nitrate and finds a high price in the arts for its uses in colouring porcelain.

When the black oxide is heated moderately in air or oxygen, it is converted into the oxide, forming the essential constituent of a pitchblende, that is, the green, or uranoso-uranic oxide U_3O_8 or $UO_2.2UO_3$. On stronger ignition the black oxide is reformed. This oxide does not form salts.

URANIC OXIDE.

FORMULA UO_3. MOLECULAR WEIGHT 288.

This oxide partakes, as we have already seen, of the characters of both an acid and a base.

According to Ebelmen, a hydrate of it, $UO_3 3H_2O$, is obtained by exposing a strong solution of uranic oxalate to the sun's rays, when a brownish-violet powder forms consisting of the green oxide in a hydrated state, U_3O_8, $3H_2O$, while carbonic anhydride is evolved. On further exposure to the air, this substance takes up oxygen and becomes transformed into a greenish-yellow mass of UO_3, $3H_2O$. From this the anhydrous oxide is obtained by heating it to a temperature of 300° C.

The salts of uranic oxide are of a bright yellow colour.

The compounds of this oxide with the earths are capable of withstanding a strong heat without decomposition; hence they are employed to give a fluorescent yellow colour to glass.

Uranates.—As already shown, uranic oxide possesses not only basic, but also acid powers of combination. The combinations with the alkali metals may be obtained by precipitation of a uranic salt with an alkali.

The potassic salt has the formula $K_2O.2UO_3,3H_2O$, while the sodic salt which is prepared as a commercial article for staining glass is represented by $Na_2O2UO_3 6Aq$. To prepare it, pitchblende is roasted with lime in a reverberatory furnace, and the resulting product, which contains calcic uranate, is decomposed by dilute sulphuric acid, giving uranic and calcic sulphates. On now heating the solution when drawn off from the calcic sulphate with sodic carbonate, sodic uranate is precipitated in an impure form; it is redissolved by excess of the alkali, and reprecipitated by dilute sulphuric acid, giving pure hydrated sodium uranate ($Na_2O.2UO_3,6H_2O$).

Of the ammonium salt, or 'uranium yellow' as it is termed, we have already spoken.

The uranates of the earth metals and heavy metals are prepared by adding ammonia to a mixture of a uranic salt and a salt of the metal desired. The double carbonates and acetates of uranium and other metals yield uranates on ignition.

ARSENIC.

Symbol As. Atomic Weight 75.

History.—Though this elementary substance was known at a very remote period, it was first accurately investigated in 1733, and its relation to white arsenic pointed out by Brandt. In 1775 arsenic acid and arsenuretted hydrogen were discovered by Scheele, and the general chemical relations of arsenical compounds were afterwards more thoroughly investigated by Berzelius.

Occurrence.—Arsenic occurs naturally to some extent among the mineral deposits in the older rocks, but it is much more frequently met with in a state of combination; either with sulphur as realgar and orpiment, with antimony as allemontite, with iron as arsenic pyrites Fe_2As_3 and arsenosiderite $FeAs_2$, with cobalt as smaltine and tesseral pyrites, with nickel as white nickel pyrites, copper nickel, and placodin; also in combination with various other metals and their sulphides, as in mispickel $FeAs_2FeS_2$, grey copper, etc.; combined with oxygen as arsenolite, and with oxygen and metallic oxides in the state of arsenates as pyromorphite, skorodite, cube ore, etc. In smaller amount and in various states of combination, arsenic also occurs in a very large number of minerals, as well as in the water of some mineral springs and in the ferruginous deposits from such water.

Characters.—Arsenic is a solid substance of a steel-grey colour and metallic lustre; it is crystalline and very brittle; its specific gravity varies from 5·7 to 5·9. When heated it does not melt, but volatilises, and in contact with atmospheric air is readily oxidised. The vapour is very poisonous, and has a characteristic odour resembling garlic. It exhibits a vapour density of 150, which is twice its atomic weight, so that its gaseous molecule like that of phosphorus occupies only one half the volume of a molecule of hydrogen. Arsenic is capable of assuming at least two distinct allotropic conditions, and its physical characters vary according to the manner in which it is sublimed. Thus, if it be strongly heated, or made to condense upon plates at a temperature slightly below that at which arsenic volatilises, so that the deposition takes place in an arsenical vapour, it takes the form of a nearly white mass, with a powerful metallic lustre. This form of arsenic, even when in the state of powder, scarcely oxidises in the air or at a temperature of 80° C. It is this form of the metal which is produced by heating arsenical pyrites.

On the other hand, the arsenic obtained by reduction of arsenous acid with charcoal takes the form of a dark grey crystalline powder of less density than the compact form o arsenic. Arsenic assumes this condition when obtained in any way in which, before condensation, its vapour is mixed with other gases. This form of arsenic oxidises readily in the air, especially at higher than normal temperatures. Arsenic combines readily with chlorine, bromine, iodine, or sulphur, especially when heated; it is oxidised by nitric acid, but is little affected by hydrochloric acid.

Native arsenic, which is sometimes definitely crystalline (indistinct rhombohedral crystals), resembles in its general characters the artificial preparation.

Preparation.—Arsenic is obtained by subjecting either the native iron arsenides $FeAs_2$ and Fe_2As_3, or mispickel $FeAs_2FeS_2$, mixed with scrap iron and lime, to the action of heat in tubular earthen retorts, by which means these substances are decomposed, and the arsenic liberated is sublimed into suitable condensers, leaving a residue of metallic iron or of ferrous sulphide. It is also prepared from the crude arsenous oxide obtained as a sublimate in roasting arsenical ores, by reducing this product with charcoal, and distilling off the arsenic from tubular retorts into condensers made of thin sheet iron rolled into the form of tubes, and connected with the mouths of the retorts with a luting of fire clay.

The furnaces employed at Ribas in Spain for extracting arsenic from mispickel are represented by figs. 370 and 371. The ore is heated in a number of horizontal tubes (*a a*) arranged on each side of the arched chamber heated by a fire on the grate (*d*).

The products of combustion pass off through the flues (*c c*) into a chimney. To the ends of the tubes projecting beyond the side of the furnace are attached the receivers (*b b*) in which the arsenic is condensed.

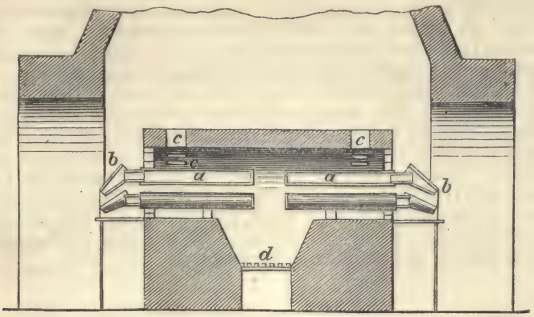


FIG. 370.

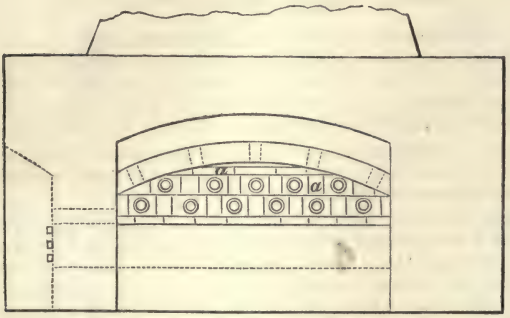


FIG 371.

At Reichenstein in Silesia similar furnaces are employed in working mispickel and arsenical pyrites, which frequently contain some gold.

Uses.—Arsenic is used principally to form an alloy with lead for making shot, as it renders the metal harder and prevents the globules from losing their spherical shape.

Compounds.—The constitution of arsenical compounds is in many instances closely analogous to that of phosphorous compounds, and in some instances to that of nitrogen compounds. With hydrogen it forms a gaseous substance AsH_3, called arsine or arsenetted hydrogen, and corresponding to ammonia and phosphine in its chemical relations. With chlorine it forms a trichloride $AsCl_3$; it also forms similar compounds with bromine, iodine, and fluorine. Besides the trivalent character which it presents in these compounds in common with nitrogen, phosphorus, antimony, and bismuth, arsenic has like them a pentavalent character in some of its compounds. For instance, there are two oxides—arsenous oxide As_2O_3, and arsenic oxide As_2O_5, the compounds corresponding to these two substances being distinguished as arsenous compounds and arsenic compounds. Both the oxides combine with water and basic oxides, forming two series of salts termed respectively arsenites and arsenates, corresponding to the phosphites and phosphates; of the two hydrogen salts of these oxides, constituting arsenous acid H_3AsO_3, and arsenic acid H_3AsO_4, the latter only is known. The normal constitution of the neutral arsenites is represented by the formula M_3AsO_3, but they are readily converted into basic or acid salts and the composition of them is only imperfectly known. The neutral arsenites of the alkalies and alkaline earths are soluble in water; most of the others are insoluble. The neutral arsenates correspond to the formula M_3AsO_4, and they are much more stable substances than the arsenites; the neutral arsenates of the alkalies are soluble in water and all the others insoluble in water, but several of them are dissolved by arsenic acid, forming monometallic acid salts which dissolve in water. The dimetallic arsenates of the

alkaline earths are also dissolved by solutions of ammoniacal salts, owing to the formation of double arsenates which are soluble in water.

Arsenic combines with sulphur in three proportions, forming a disulphide As_2S_2, which occurs naturally as realgar; a trisulphide As_2S_3, which occurs as orpiment, and a pentasulphide As_2S_5. The two latter correspond to arsenous oxide and arsenic oxide, and they both combine with basic sulphides, forming two series of saline compounds termed sulpharsenites and sulpharsenates, many of which correspond in constitution with the oxygen salts, sulphur taking the place of oxygen. Only the disulphide and the trisulphide or arsenous sulphide are known in the uncombined state.

Arsenic unites readily with many metals when melted with them, forming alloys which are generally brittle and very fusible; it also forms definite compounds with metals, which are termed arsenides, and many of these substances occur naturally either as distinct minerals, such as smaltine CoA_2, tesseral pyrites $CoAs_3$, white nickel pyrites $NiAs_2$, copper nickel NiAs, placodin Ni_2As, arsenosiderite Fe_2As_3, arsenic pyrites $FeAs_2$; or associated with sulphides, as in cobaltine $CoAs_2CoS_2$, nickel glance $NiAs_2NiS_2$, mispickel $FeAs_2FeS_2$, and the various kinds of fahl ore and arseniferous pyrites, etc.

ARSENOUS OXIDE.

Formula As_2O_3. Molecular Weight 198.

History.—This substance was first distinctly mentioned by Geber, as the product obtained by oxidation of arsenous sulphide, and subsequently by Avicenna and Basil Valentin, as *arsenicum album*. It was long considered to contain sulphur, and this opinion was first disputed by Kinkel in 1677; but it was not recognised to be an oxide until the year 1787, and in 1800 Fourcroy gave it the name of arsenous acid.

Occurrence.—Arsenous oxide occurs naturally to some extent as arsenite, together with ores of nickel and cobalt, but it is chiefly obtained as an accessory product in the treatment of ores containing arsenical compounds.

Characters.—Arsenous oxide is a solid white substance which crystallises in two distinct forms, and is also capable of assuming an amorphous or vitreous condition. Octahedral arsenous oxide has a specific gravity of 2·695, and is the most stable form of this substance; the prismatic variety is converted into the octahedral form by sublimation and by solution in water; the vitreous oxide has a specific gravity of 3·74; it gradually passes into the octahedral form.

Arsenous oxide volatilises at about 218°, forming a dense colourless vapour the specific gravity of which is 13·85 as compared with atmospheric air. The vapour has no smell. The crystalline oxide sublimes without melting, but the vitreous oxide melts before volatilising to any great extent. Arsenous oxide dissolves sparingly in water, requiring 10 or 12 times its weight of hot water and about 30 parts of cold water; the vitreous oxide dissolves more readily than the crystalline variety. The solution reddens litmus paper slightly. Dilute acids dissolve arsenous oxide more copiously than water with aid of heat, but greater part of the oxide crystallises out as the solution cools.

Arsenous oxide readily gives up its oxygen to oxidisable substances, and is decomposed in this way when heated with carbon, sulphur, phosphorus, sodium, or zinc, with liberation of arsenic. The vapour brought into contact with red-hot lime is decomposed, and arsenic liberated, while calcium arsenate is formed; at a lower temperature part of the arsenous oxide combines with the lime, forming calcium arsenite. A similar result is produced by heating arsenous oxide with potassium carbonate.

Arsenous oxide is converted into arsenic oxide by nitric acid, chromic acid, hypochlorous acid and other substances capable of giving up oxygen; it is, therefore, a powerful reducing agent.

Arsenous oxide combines with basic oxides, forming a series of saline compounds called arsenites, in which it acts the part of an acid. The hydrate or hydrogen salt is not known, but it is probably tribasic, and most of the salts have the following formulæ:

Trimetallic salts	M_3AsO_3	or $M''_3 2AsO_3$
Dimetallic salts	M_2HAsO_3	or $M''HAsO_3$
Monometallic salts	MH_2AsO_3	or $M''H_4 2AsO_3$

Some of the arsenites have a composition represented by the formula $2M_2O.As_2O_3$, or $M_4As_2O_5$, and acid salts $M_2O.2As_2O_3$ and $2M_2O.3As_2O_3$.

Ammonium arsenite NH_4AsO_3 is crystalline and sparingly soluble; it is very readily decomposed by contact with atmospheric air.

Potassium arsenites.—The monopotassic salt $2KH_2AsO_3.As_2O_3$ obtained by digesting arsenous oxide with potassium carbonate solution at 100° forms prismatic crystals which give off water at 100°, and are converted into a compound of pyro-arsenite with arsenous oxide $K_2H_2As_2O_5.As_2O_3$; this when heated more strongly gives off water, melts to a yellow liquid which solidifies on cooling, and consists of metarsenite combined with arsenous oxide $2KAsO_2.As_2O_3$ or $K_2O2As_2O_3$.

Sodium arsenites are formed by the reaction of arsenous oxide with sodium carbonate in the same manner as the potassium salts, but their composition has not been so fully determined.

Preparation.—Arsenous oxide is prepared in some places by roasting either mispickel or arsenical pyrites in a kind of muffle furnace, so that the powdered ore is exposed at a high temperature to the oxidising action of atmospheric air, without coming in contact with the products of combustion furnished by the fuel used. At Altenberg in Saxony and Reichstein in Silesia this operation is carried out on a large scale, and the vapour of arsenous oxide is condensed in spacious chambers connected with the muffles. The furnaces used for this purpose are represented in transverse and longitudinal sections by figs. 372 and 373. The muffle (*a*) is inclined upwards

Fig. 372.

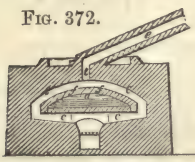
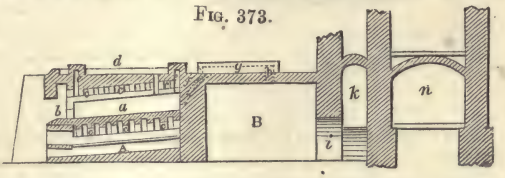


Fig. 373.



from the mouth of the furnace (*b*) and is heated by flues (*c c c*) passing round it and communicating with the smoke flue (*e*) and with the fireplace (A). The arsenous oxide vapour passes off through two flues (*f f*) shown in the ground plan, fig. 375, into two other flues (*g g*), both terminating in the flue (*k*) which conducts the vapour into the vault (B); it then passes through the opening (*i*) into the chamber (*k*) and through the opening (*l*) into the lower chambers (*m n*) of a condensation tower represented in vertical section by fig. 374. This is divided into several compartments

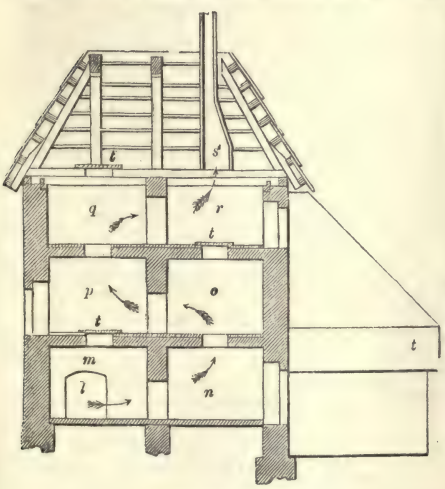


Fig. 374.

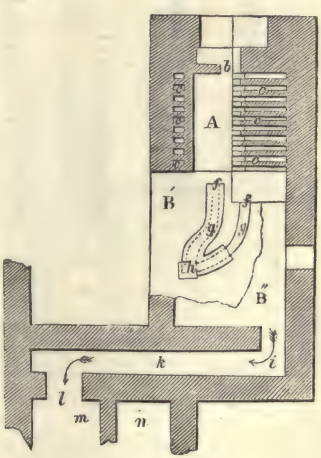


Fig. 375.

(*m n o p q r*); here the arsenous oxide is deposited in the state of a fine powder and the uncondensable gas passes away through the chimney (*s*). When the operation is completed the covers (*t t*) on the floor of the chambers are removed for the purpose of transferring the arsenous oxide into the lower chambers of the tower. The residue left in the muffle contains ferric arsenate, together with the silicious portion of the ore, and it is either thrown away, or in some instances treated for the extraction of gold and silver.

Very frequently arsenous oxide is obtained as a by-product in the roasting of various ores containing arsenical minerals, and then it is condensed from the gaseous products by passing them through a series of flues connected with the roasting furnaces.

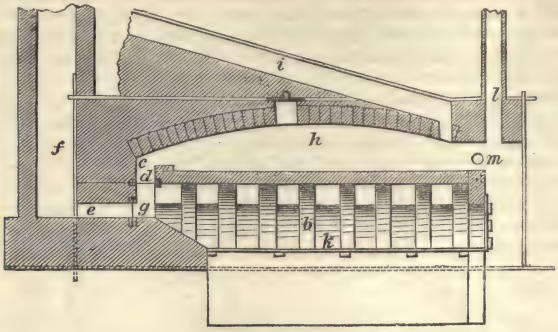


FIG. 376.

The furnaces used in this case are sometimes constructed so that the flame can be admitted into the roasting chamber, or excluded at will. Fig. 376 represents a furnace of this kind used at Ribas in Spain, for roasting arsenical pyrites. The hearth (*a*) is supported on cross walls (*b*) between which the flame from the fire grate (*k*) plays against the lower surface. The opening (*c*) at the end of the hearth can be closed by a sliding damper (*d*) and the flame is then made to pass into the chimney (*f*) through the flue (*e*). If it be desired to admit the flame into the roasting chamber, the flue (*e*) is closed by a damper (*g*) and the draught then passes across the hearth to the flue (*i*). Above the mouth of the furnace is a vertical flue (*l*) through which any arsenical vapour escaping from the chamber passes off.

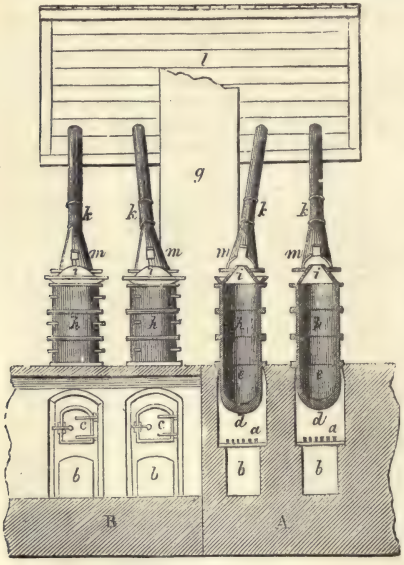


FIG. 377.

The pulverulent arsenous oxide obtained in either case, requires to be refined and converted into a marketable condition; for this purpose it is sublimed in cast-iron pots surmounted by cylinders of the same material. The general arrangement of the apparatus is represented by figs. 377 and 378. The iron pots (*e e*) for heating the arsenous oxide are set over separate fireplaces (*d d*) fitted with doors (*c c*) and having flues (*f f*) leading to a common chimney (*g*). Above the pots are the iron cylinders (*h h*) covered with the caps (*i i*), and pipes (*k k*) leading to the chamber (*l*); at the lower part of these pipes there are openings (*m m*) for introducing an iron rod.

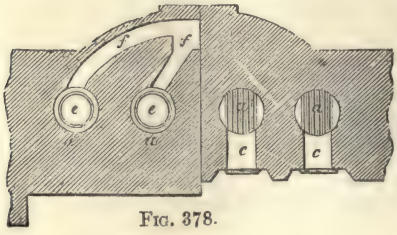


FIG. 378.

According to the temperature at which the operation is conducted, the sublimed arsenous oxide is obtained in the state of a loose friable mass or as a hard vitreous cake.

The following table gives the composition of arsenous oxides obtained from the roasting of tin ores at Altenberg.

Arsenous oxide	90·10	95·95	94·31	98·20
Arsenous sulphide	2·05	0·32	1·03	—
Bismuth	—	—	0·25	—
Sulphur	0·13	0·71	0·50	—
Antimonous oxide	—	—	—	1·68
Ore	6·55	2·79	3·21	—

ARSENIC OXIDE.

Formula As_2O_5. Molecular Weight 230.

History.—This substance was first prepared by Scheele in 1775; but some of its compounds were known long before that time, and the preparation used in medicine by Paracelsus under the name of *arsenicum fixum* was potassium arsenate obtained by heating arsenous oxide with nitre. Macquer also in 1744 found that the residue left in preparing nitric acid according to Glauber's method by distilling nitre with arsenous oxide, contained a crystallisable salt, and in 1798 by heating white arsenic with sulphuric acid he obtained a fixed vitreous substance which was probably the hydrate of arsenic oxide; prior to 1764 Cavendish had studied this substance, to which he gave the name of arsenical acid.

Occurrence.—Arsenic oxide does not occur naturally in the free state; but it often occurs in combination with lime as pharmacolite $2CaHAsO_4 + 5H_2O$ and as haidingerite $2CaHAsO_4 + H_2O$, with ferric oxide as iron cinder $2Fe_2O_3.As_2O_5 + 12H_2O$, as scorodite $Fe_2O_3As_2O_5 + 4H_2O$, as pittizite $2Fe_2O_3.As_2O_5 + 12H_2O$, and with ferrous and ferric oxides as cube ore $FeO.Fe_2O_3.As_2O_5 + 6H_2O$; with lead oxide and lead chloride as pyromorphite $3PbO.As_2O_5.PbCl_2$, with lime and magnesia as picropharmacolite $CaHAsO_4.MgHAsO_4 + 2CaMg_3AsO_4 + 5H_2O$, with cobaltous oxide as cobalt bloom $Co_3AsO_4 4H_2O$, and with cupric oxide as olivinite $4CaOAs_2O_5 + H_2O$, as well as in various other minerals.

Characters.—Arsenic oxide is a white substance nearly insoluble in water, but it gradually combines with water, forming a soluble hydrate; it is decomposed at a full red heat into arsenous oxide and oxygen; it is also decomposed when heated to redness with carbon, metals, potassium cyanide, etc., yielding metallic arsenic.

The compound of arsenic oxide with water $As_2O_5 3H_2O = 2H_3AsO_4$ is called arsenic acid, and is the representative of a series of saline compounds called arsenates, consisting of arsenic oxide combined with various basic oxides. The normal or neutral arsenates contain three atomic proportions of monovalent metals to one atomic proportion of arsenic, or three of divalent metals to two of arsenic, and their composition is represented by formulæ corresponding to that of arsenic acid H_3AsO_4; thus, for instance, potassium arsenate is K_3AsO_4, calcium arsenate is $Ca_3 2AsO_4$ and ferric arsenate $FeAsO_4$. There are also two series of acid arsenates in which only part of the hydrogen of arsenic acid is replaced by a metal; the acid sodium arsenates have the formulæ Na_2HAsO_4 and NaH_2AsO_4; the corresponding barium salts are $BaHAsO_4$ and $BaH_4 2AsO_4$. The arsenates are isomorphous with the corresponding phosphates.

Arsenic acid H_3AsO_4 is a crystallisable substance readily soluble in water. It may be prepared by heating arsenous oxide with nitric acid of 1·35 specific gravity in sufficient quantity to oxidise the arsenous oxide; a syrupy liquid is thus obtained which by standing deposits crystals containing two molecules of the acid and one molecule of water of crystallisation $2H_3AsO_4 + H_2O$; these crystals are very deliquescent, and when heated to 100° they melt, lose the water of crystallisation, and are converted into a crystalline powder consisting of H_3AsO_4. This substance may also be obtained in large crystals by exposing a concentrated solution of arsenic acid to a very low temperature. Another hydrate of arsenic oxide $As_2O_5 2H_2O = H_4As_2O_7$ is obtained by heating the hydrated crystals of arsenic acid to a temperature ranging from 140° to 160°; it separates in hard shining crystals which dissolve in water with great increase of temperature. By heating these crystals to 200° for some time, and then raising the temperature to 206°, water is given off, the mass suddenly becomes pasty, and is converted into a white flaky monohydrate $HAsO_3$ which dissolves slowly in cold water. These hydrates of arsenic oxide correspond to the hydrates of phos-

phoric oxide, but differ from them in being at once converted into the ordinary trihydrate when dissolved in water.

Ammonium arsenate $3NH_4.AsO_4$ is a soluble pulverulent substance obtained by saturating strong ammonia solution with arsenic acid; it is decomposed by heat and converted into the acid salt $2NH_4.HAsO_4$, which crystallises in prisms that effloresce in the air, giving off half their ammonia; this salt when heated is decomposed, yielding ammonia, water, metallic arsenic, and nitrogen. The salt $NH_4H_2AsO_4$ is very soluble in water and has a strong acid reaction; it crystallises in octahedra, is very deliquescent, and is decomposed by heat like the last mentioned salt.

Barium arsenate Ba_32AsO_4 is insoluble in water; the acid salt BaH_42AsO_4 is soluble in water and crystallisable, and the intermediate salt $BaHAsO_4$ obtained as a precipitate by adding solution of disodic arsenate to barium chloride is readily convertible into the two salts first mentioned; it combines with ammonia, forming a crystalline precipitate having the composition represented by the formula $Ba.NH_4AsO_4$.

Calcium arsenates correspond in composition and characters with the barium salts, and some of them occur naturally.

Cobaltous arsenate Co_32AsO_4 occurs naturally in a hydrated state, as cobalt bloom, in red crystals, and as prepared by precipitating cobalt salts with sodium arsenate it is a reddish powder.

A basic cobaltous arsenate known by the name of *chaux métallique* is used as a pigment; it is prepared either by adding potassium carbonate to a solution of cobalt glance in nitric acid as long as ferric arsenate is precipitated, and then precipitating the cobaltous arsenate from the filtered solution; or by melting cobalt glance with twice its weight of potash and some sand, extracting the cold mass with water, and again melting the insoluble portion with potash; by this means a blue slag is obtained together with cobalt arsenide, which can be converted into the basic arsenate by careful roasting.

Cupric arsenate Cu_32AsO_4 is a green powder, soluble when freshly precipitated in ammonia, forming upon evaporation of the liquid crystals which are decomposed by exposure to light; they have a composition represented by the formula $Cu4NH_42AsO_4 + 2(NH_4HO)$. Several basic cupric arsenates occur naturally.

Ferrous arsenate Fe_32AsO_4 is a white pulverulent substance which acquires a greenish colour when exposed to the air.

Ferric arsenate $FeAsO_4$ occurs naturally in the hydrated state as scorodite, cube ore, and in other minerals. The precipitate formed by adding disodic arsenate to ferric chloride solution dissolves in ammonia, and on evaporating the solution gives a ruby red mass consisting of ammonio-ferric arsenate.

Lead arsenate Pb_32AsO_4 is a white insoluble powder that turns yellow and cakes together when heated, but does not melt. This salt occurs in some varieties of pyromorphite in the place of lead phosphate.

Magnesium arsenates correspond in composition and characters with the calcium salts; the acid salt MgH_42AsO_4 is readily soluble and forms a gummy mass in the dry state. Ammonio-magnesic arsenate $MgNH_4AsO_4 + 6H_2O$ is formed as a crystalline precipitate on adding an ammoniacal solution of arsenic acid to the solution of a magnesium salt mixed with ammonium chloride; it is almost insoluble in water, containing ammonia like the corresponding ammonio-phosphate. Double salts consisting of magnesium arsenates and calcium arsenates occur naturally as picropharmacolite, and corresponding salts containing potassium or sodium arsenates may be formed artificially.

Nickel arsenate Ni_32AsO_4 occurs naturally as nickel bloom; artificially prepared it is a pale green powder soluble in strong acids and in ammonia.

Potassium arsenate K_3AsO_4 is a very soluble salt, crystallisable in small needles which deliquesce rapidly on exposure. Of the acid arsenates the salt K_2HAsO_4 is a deliquescent non-crystalline mass, and the salt KH_2AsO_4 forms crystals permanent in the air; it dissolves in about 6 parts of cold water and a smaller proportion of hot water, but is insoluble in alcohol.

Silver arsenate Ag_3AsO_4 is formed by mixing soluble arsenates with a solution of silver nitrate as a dark brown precipitate which melts when heated, is converted into chloride by hydrochloric acid, and is soluble in acetic acid or ammonia. This salt dissolves in solution of arsenic acid, and on evaporation of the solution the monargentic salt AgH_2AsO_4 is deposited.

Sodium arsenate Na_3AsO_4 is soluble in water, and crystallises with 12 molecules of water in rhombic prisms which are permanent in the air and melt at 86°. The disodic salt Na_2HAsO_4 is also soluble, and forms crystals with 12 molecules of water, which effloresce and are isomorphous with ordinary sodium phosphate. A more concentrated solution kept at a temperarure of 20° gives crystals containing 14 molecules of water, which are not efflorescent.

The monosodic salt NaH_2AsO_4 is more soluble than the disodic salt, and forms large crystals isomorphous with the corresponding phosphate.

The double sodic and ammonic arsenate $NaNH_4HAsO_4 + 4H_2O$, obtained by mixing solutions of the disodic and diammonic salts, forms crystals resembling those of the corresponding phosphate known as microcosmic salt.

Zinc arsenate Zn_32AsO_4 occurs naturally combined with 8 molecules of water as köttigite; on adding a solution of sodic arsenate to zinc acetate this salt is obtained as a white precipitate which dissolves in excess of arsenic acid, and on evaporating the solution crystals of an acid salt are deposited.

ARSENIC DISULPHIDE.

Formula As_2S_2. Molecular Weight 214.

History.—This substance, commonly called realgar, was known at a very remote period, and was mentioned by Aristotle, Theophrastus, and Dioscorides under the name *σανδαράκη*, by Latin writers as *sandaraca*.

Occurrence.—Arsenic disulphide occurs naturally in the form of oblique rhombic prisms of an orange yellow or reddish colour, accompanying ores of lead and silver.

Characters.—As prepared artificially by melting metallic arsenic with sulphur the disulphide is of a ruby colour, transparent, easily fusible, and it solidifies to a crystalline mass. It burns in the air with a blue flame, yielding sulphurous oxide and arsenous oxide.

Arsenic disulphide combines with basic sulphides, forming saline compounds called hyposulpharsenites, which are sparingly soluble in water.

ARSENOUS SULPHIDE.

Formula As_2S_3. Molecular Weight 246.

History.—The term *ἀρσενικὸν* was probably first used by Dioscorides to indicate this substance as distinguished from the red sulphide, and though at a later period the difference in external characters between these substances was recognised, they were often regarded as being in common with white arsenic merely modifications. It was not until 1801 that Proust showed that orpiment, or the yellow sulphide, did not contain oxygen.

Occurrence.—Arsenous sulphide occurs naturally as orpiment, and in combination with basic sulphides it is a constituent of a great number of minerals.

Characters.—Arsenous sulphide has a fine yellow colour, is insoluble in water and dilute acids, melts at a moderate heat and is volatilisable. The crystalline form of the native sulphide is the rhombic prism. The specific gravity is 3·48. When heated in contact with atmospheric air it burns and by oxidation is converted into arsenous oxide and sulphurous oxide. Chlorine converts it into a brown liquid consisting of arsenic sulphochloride; nitric acid or nitromuriatic dissolves it with oxidation; by fusion with acid potassium sulphate it is converted into potassium arsenite and sulphurous oxide is given off:

$$12KHSO_4 + As_2S_3 = 3K_2SO_4 + 12SO_2 + 6H_2O + 2K_3AsO_3$$

When the vapour is brought into contact with red-hot lime, calcium arsenate is formed, together with calcium sulphide:

$$As_2S_3 + 6CaO = 3CaS + Ca_3As_2O_6,$$

and is attended by the conversion of the arsenate into arsenite and arsenic is given off:

$$5Ca_3As_2O_6 = 3Ca_3As_2O_8 + 6CaO + 4As.$$

Arsenous sulphide combines with basic sulphides forming the saline compounds called sulpharsenites, of which there are three series represented by the potassium salts $3K_2S.As_2S_3$ or K_3AsS_3, $2K_2S.As_2S_3$ or $K_4As_2S_5$, and $K_2S.As_2S_3$ or $KAsS_2$. The alkaline salts are soluble in water, but the solutions are decomposed by evaporation.

ANTIMONY.

Symbol Sb. Atomic Weight 122.

History.—This elementary substance was first definitely described by Basil Valentin towards the end of the fifteenth century, but it was probably known at an earlier period. It was at first regarded as a variety of lead, and likewise as containing iron, or as being in some way subject to planetary influences in its production.

Occurrence.—Antimony occurs to some extent naturally in the metallic state and in the form of alloys with other metals; in various states of combination it occurs more frequently—the sulphide as grey antimony or stibnite, the oxides as antimony bloom, valentinite or senarmontite, and as antimony ochre or cervantite. The sulphide also occurs in combination with several other sulphides, as berthierite, zinkenite, miargyrite, bournonite, pyrargirite, grey copper, etc., and in combination with antimonous oxide as red antimony or kermesite.

Characters.—Antimony is a bluish-white metal of high lustre and very crystalline structure; it is very brittle, and the density varies from 6·702 to 6·860; it melts at 450°, and volatilises at a higher temperature. Antimony is not sensibly oxidised by exposure to atmospheric air at ordinary temperatures, but it oxidises readily when melted. At a red heat it takes fire and burns with a white flame, giving rise to white fumes of antimonous oxide.

Antimony is oxidised by nitric acid, but is not dissolved; by moderately dilute acid it is converted chiefly into antimonous oxide, and only a small proportion of antimonic oxide is formed, but with strong nitric acid the product is chiefly antimonic oxide. Antimony is not acted upon by dilute sulphuric acid, but when heated with strong sulphuric acid it is oxidised, sulphurous oxide is given off, and antimonous sulphate is formed. In the compact state antimony is not dissolved by hydrochloric acid, but when the powder is heated with hydrochloric acid, it is dissolved with evolution of hydrogen.

When in the form of powder antimony is dissolved by a solution of an alkaline polysulphide, while the metals usually associated with it are left undisturbed.

When certain solutions of antimony are subjected to electrolysis, the metal is deposited in an amorphous form with properties differing according to the nature of the solution employed and the mode of deposition. A deposit having an explosive property is obtained by using weak currents of constant strength and concentrated acid solutions. When deposited from the chloride, the amorphous antimony has a density of 5·8; if heated to 77° and up to 99° sudden evolution of heat occurs with violence. The metal deposited from the bromide has a sp. gr. of 5·44, and at 121°, if touched with a red-hot wire, it gives out heat with explosive violence. The variety deposited from the iodide has a sp. gr. of 5·25, and gives out less heat than the other forms.

Preparation.—Antimony is obtained entirely from the sulphide, either by converting it into oxide by roasting, and then reducing the oxide by heating with carbonaceous materials, or by melting the sulphide with metallic iron or charcoal and alkalies. When iron is used for the purpose of extracting antimony from the sulphide, it should be either in the spongy state or in the form of filings. The operation is conducted either in crucibles or in reverberatory furnaces. The reduction by metallic iron takes place according to the following equation: $Sb_2S_3 + 3Fe = 2Sb + 3FeS$.

The whole of the sulphur is separated from antimonous sulphide by iron at a moderate heat, but a higher temperature is requisite for melting the ferrous sulphide so as to enable the antimony to separate from it and form a distinct layer; at this high temperature the antimony is liable to oxidation, and to prevent this, the mass must either be covered with charcoal or some sodium carbonate must be added to the materials, and the double sulphide of iron and sodium thus formed melts more readily. These two methods of extraction may be briefly described as follows:—

In the first the sulphide is roasted in a reverberatory furnace until the sulphur is expelled, and a grey mass consisting mainly of teroxide of antimony results: $Sb_2S_3 + 9O = Sb_2O_3 + 3SO_2$. During this operation the charge of stibnite requires constant raking or stirring, to bring every part in contact with the oxygen of the air, which mixed with the flame plays over its surface. Meanwhile care must be taken that the temperature shall not rise above a given extent; otherwise sulphide of antimony volatilises and causes a serious loss in the process.

The product obtained in this way is now mixed with one tenth its weight of crude tartar and the mixture reduced in large earthen crucibles placed in a wind furnace. The following equation represents the change which here takes place:

$$Sb_2O_3 + 2KC_4H_5O_6 = 2Sb + K_2CO_3 + 7CO + 5H_2O.$$

Sometimes however this reduction is effected by mixing the crude oxide of antimony with one sixth of its weight of charcoal, and making the whole into a paste with a strong solution of potassic carbonate. In either case the metal collects at the bottom of the crucibles, and above it there forms a scoria which consists chiefly of antimonic, sodic, or potassic sulphide, which is known in the arts as crocus of antimony. Sometimes the metal is re-washed with the scoria. In the process it is estimated that three sevenths of the total amount of antimony is lost. The metal obtained in this way is not pure, but is nevertheless ready for the market; its principal impurity is iron.

Figs. 379 and 380 illustrate the construction of a furnace which was used at Linz, in Germany, for reducing the sulphide by one operation. The bed is concave, and is formed of sand and clay; through the pipe (*a*) the fused metal flows out as soon as it is produced; (*b*) is an air channel in the bridge (*d*). The charge is introduced

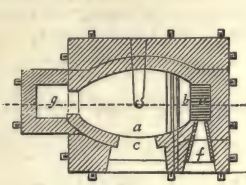


Fig. 379.

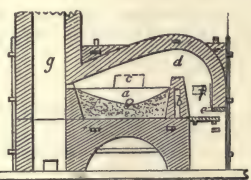


Fig. 380.

through the door (*c*), and through the same opening the residuary slag is removed; the fire is shown at (*f*); (*e*) is the grate, and (*g*) the chimney.

In the English process of obtaining metallic antimony there are three distinct operations, termed singling, doubling, and melting for star metal.

1. *Singling.*—About 40 lbs. of the ore, broke up into lumps, are introduced into a red-hot crucible with a quantity of slag produced from the *doubling* operation. Above this mixture there is placed a mass of iron which generally takes the form of a cone, consisting of old tin plate, 20 or 22 lbs. of which constitute a charge. When the charge of ore and slag has melted, the iron is pressed down into the mass and reduction thus effected. Each fusion requires about 1½ hours, and at its termination the molten mass is poured into a conical mould; when sufficiently cold, the antimony is separated from the ferruginous mass covering it.

Doubling.—The impure metal from the first operation is next fused in a similar crucible with the addition of a little sulphate of sodium and a small quantity of slag from the third operation, 80 lbs. of crude metal, and 2 of salt cake being the proportions employed. The fusion lasts nearly 10½ hours and gives bowl metal.

Refining, Frenching, or Melting for Star Metal.—About 60 lbs. of bowl metal are broken into fragments and mixed with 2 lbs. of pearl ash or American potash and 5 lbs. of slag obtained from a previous similar operation. The mass is melted in less than an hour, and the refined metal is cast into rectangular ingots, care being taken to cover each one with slag. In this way the metal crystallises, owing, as Matthieson has shown, to the presence of some little impurity.

Uses.—Antimony is too brittle to be of much value when used alone, but its alloys are widely employed; such are type metal, Britannia metal, plate pewter, etc. Antimony is also used for hardening bullets and shots, etc.

Compounds.—Antimony forms two series of compounds in which it is respectively trivalent and pentavalent, as in the chlorides $SbCl_3$ and $SbCl_5$, or the oxides Sb_2O_3 and Sb_2O_5. There are some compounds intermediate between these, as, for instance, the oxide SbO_2, which may be regarded as containing antimonic oxide

combined with antimonous oxide $Sb_2O_3 + Sb_2O_5 = 4SbO_2$. Both the oxides combine with water and basic oxides, forming two series of salts, termed respectively antimonites and antimonates; the former are very unstable, but the latter are in many instances well-defined salts. Antimonous oxide also acts the part of a feeble base, forming compounds with sulphuric, nitric, and tartaric acids.

The salts formed from antimonous oxide when in solution, and largely diluted with water, give a milky deposit of basic compounds, which are, however, soluble in tartaric acid.

Antimony unites with most other metals when melted with them, forming alloys which are hard and brittle; some of these compounds occur naturally, as for instance dicrasite or antimonial silver Ag_4Sb and Ag_6Sb in the form of six-sided prisms of a silver-white colour. Nickel antimonide Ni_2Sb occurs naturally as breithauptite in thin hexagonal plates. A compound of antimony with arsenic occurs naturally as allemontite. Antimony and lead unite readily in all proportions, the hardness and other characters of the alloys varying according to the relative proportions of the metals. The alloy, consisting of equal proportions of lead and antimony, is brittle and sonorous; when the antimony amounts to only one twelfth the weight of the lead, the alloy is malleable and somewhat harder than lead. Type metal is an alloy of lead containing from 17 to 20 per cent. of antimony. One sort of type metal consists of tea lead 75 parts, antimony 20 parts, block tin 5 parts; another kind is composed of tea lead 70 parts, antimony 25 parts, block tin 5 parts.

Stereotype metal consists of 6 parts of lead, 1 part of antimony, and sometimes a little block tin is added.

Of Britannia metal there are various varieties, the best being composed as follows:—tin 150 lbs., antimony 10 lbs., copper 3 lbs. Bismuth and zinc are sometimes added in small proportions. Alloys of antimony with tin, or with tin and lead or copper, are used in place of zinc metal for the bearings of machinery.

ANTIMONOUS SULPHIDE.

Formula Sb_2S_3. Molecular Weight 340.

History.—This substance was known at a very early period under the name of *stibium*, and subsequently among German alchemists as spiess glass, on account of its acicular crystalline structure, and of its furnishing a glassy product when partially roasted and exposed to a strong heat. It was also termed *antimonium*, and it has been fancifully supposed that this name was adopted to indicate the poisonous effects produced by it and its preparations upon the monks to whom Basil Valentine administered it medicinally.

Occurrence.—Antimonous sulphide occurs naturally in large quantities as stibnite or antimony glance in the older rock formations, and it is the principal ore of antimony. It occurs sometimes combined with antimonous oxide as red antimony ore and with ferrous sulphide as berthierite. It also occurs in combination with various other sulphides such as lead sulphide, cuprous sulphide, silver sulphide, etc., constituting sulphantimonites, which are frequent ingredients of the ores of lead, silver, and copper.

Characters.—Native antimonous sulphide is a steel-grey crystalline substance that is readily fusible and volatilisable at a very high temperature. Its sp. gr. is 4·62.

It is this substance which constitutes the crude antimony of commerce. When heated in contact with atmospheric air it burns with a blue flame, sulphurous oxide and antimonous oxide being formed:

$$Sb_2S_3 + 9O = 3SO_2 + Sb_2O_3.$$

Antimonous sulphide prepared by precipitation with acids from solution of alkaline sulphantimonites is a brownish-red pulverulent substance, having a sp. gr. of 4·15. A mixture of the amorphous sulphide with antimonous oxide, known by the name of mineral kermes, is prepared in a variety of ways for medicinal purposes. When melted, the amorphous sulphide becomes black; and, if slowly cooled, it assumes a crystalline condition. Antimonous sulphide is obtained in the hydrated state by passing sulphuretted hydrogen through an acid solution of antimonous chloride; it has a fine orange colour, which becomes darker when the precipitate is dried and moderately heated.

When kermes' mineral is digested for some time with tartaric acid, any antimonous oxide or potassium salt which may be present is dissolved, and the pure tersulphide remains.

This sulphide may also be obtained in crystals, by melting antimonous oxide and sulphur together, $2Sb_2O_3 + 9S = 2Sb_2S_3 + 3SO_2$.

Antimonous sulphide combines with basic sulphides forming a series of saline compounds called sulphantimonites; the most important of those which are prepared artificially are the alkaline salts called liver of antimony which are obtained by melting mixtures of antimonous sulphide with alkaline carbonates, or alkaline sulphates and charcoal; or by melting metallic antimony with alkaline sulphates. In the melted state these substances are black or dark brown and crystalline. They dissolve in water, but when the solutions are mixed with a very large proportion of water the sulphantimonite is deposited in a gelatinous state.

Preparation.—Antimonous sulphide is obtained by heating the native ore sufficiently to melt the sulphide and separate it from the gangues with which it is associated in the native state. This operation is carried out either in crucibles or closed cylindrical vessels heated externally. One of the simplest forms of apparatus for this purpose is represented by fig. 381. The large crucible (*b*) is filled with the ore from which the sulphide is to be extracted; holes are pierced in the bottom so that the melted sulphide runs out into a smaller crucible (*c*) placed beneath. A number of these crucibles are arranged in this way side by side between two walls (*a a*), and a fire is made in the intervening space at *e e*.

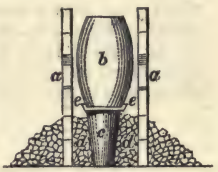


FIG. 381.

The liquation of crude antimony is effected at Malbosc, in the department of the Ardèche, in an apparatus of which the figure (382) represents a vertical section.

The mineral is placed in large earthen pots (R) of which four are set in one furnace. At the bottom of each an aperture is left, and this corrresponds with one in the tile upon which each pot rests. Beneath these in the chambers (C) are placed earthen pots (P) into which the melted sulphide flows as it descends from the cylinders.

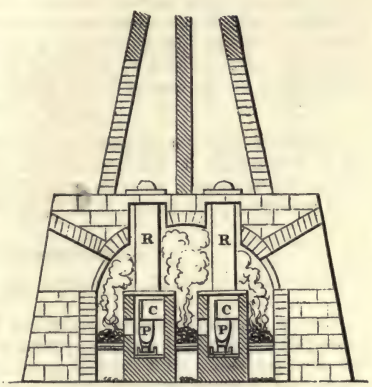


FIG. 382.

Owing to the fusible nature of sulphide of antimony, this process of liquation is one which is easily conducted, and gives little trouble.

Fir wood constitutes the fuel employed.

In England a reverberatory furnace has sometimes been employed instead of the plant described above.

Uses.— The artificial sulphide is used to some extent as a red pigment which is sold under the name of *antimony vermilion*. It is prepared by pouring solution of antimonous chloride in hydrochloric acid into one of calcic thiosulphate (hyposulphite); on heating to 60° C. the antimony vermilion is deposited.

Kermes' mineral is still largely used as a medicine in England, particularly for veterinary purposes. It may be prepared in many ways, the oldest and one of the best being as follows. The powdered sulphide is boiled with a solution of potassic carbonate or caustic potash, when it dissolves, and on cooling the filtered liquid, Kermes is deposited as a reddish-brown substance.

ANTIMONIC SULPHIDE.

FORMULA Sb_2S_5. MOLECULAR WEIGHT 404.

This body, known sometimes as sulphantimonic acid, may be obtained by passing sulphuretted hydrogen through an acid solution of antimonic pentachloride. It forms an anhydrous, orange-yellow precipitate, and has a remarkable facility of inter-combination with the sulphides of the alkali metals, forming a series of saline compounds called sulphantimonates. The composition of these salts may be represented by that of trisodic sulphantimonate $3Na_2S,Sb_2S_5 = 2Na_3SbS_4$. This compound may be obtained as a crystalline salt with 9 molecules of water.

The medicinal effects of this sulphide are more active than those of kermes, and it is used as an alternative in chronic diseases of a rheumatic and cutaneous nature, as well as in liver complaints.

ANTIMONOUS OXIDE.

FORMULA Sb_2O_3. MOLECULAR WEIGHT 292.

As previously stated, this substance is found to some extent as a mineral (valentintite or antimony bloom). It was well known to Basil Valentine, who named it *flores antimonii*.

It may be prepared in several ways, the best of which is by boiling powdered metallic antimony mixed with excess of strong sulphuric acid to dryness; there is thus formed an insoluble sulphate, while sulphurous anhydride is evolved. The last traces of acid are removed by washing first with water, and then with dilute sodic carbonate, when the oxide remains behind as a white powder.

On heating, it assumes a yellow colour, but becomes again white on cooling. It may be melted in closed vessels, and is volatile at a high temperature; the vapour which thus forms condenses in brilliant needles similar to those obtained in the same way from arsenous oxide.

On burning it in the air, it forms antimony tetroxide. It is freely soluble in hydrochloric and tartaric acid, but is oxidised to a higher form by nitric acid. It is also soluble in acid tartrate of potassium, forming tartar emetic.

ANTIMONIC OXIDE.

FORMULA Sb_2O_5. MOLECULAR WEIGHT 324.

Antimonic oxide may be obtained by oxidising the metal with nitric acid, and expelling the acid at a temperature below red heat. It is pale yellow in colour, and insoluble in water. If subjected to a strong heat it loses oxygen and forms antimony tetroxide Sb_2O_4, and this on treatment with hydric potassic tartrate (cream of tartar) forms tartar emetic, and antimonic anhydride is left undissolved:

$$2Sb_2O_4 = Sb_2O_3 + Sb_2O_5.$$

Antimonic acid forms definite compounds with the alkali metals. Thus, on boiling it with potash, it dissolves, and on the addition of an acid, hydrated antimonic acid is deposited as a white powder, Sb_2O_5, $4H_2O$.

The normal potassic salt is $K_2Sb_2O_6$, $5H_2O$.

ANTIMONOUS CHLORIDE.

FORMULA $SbCl_3$. MOLECULAR WEIGHT 228·5.

This substance, formerly known as *butter of antimony*, owing to its fusible nature, may be obtained in the anhydrous condition by distilling a mixture of eight parts corrosive sublimate with three of powdered antimony, when a reaction indicated by the following equation results: $Sb_4 + 4HgCl_2 = 2SbCl_3 + Sb_2Hg_2 + Hg_2Cl_2$, that is to say, terchloride of antimony distils over, while an alloy of antimony and mercury and calomel remain behind. Or the chloride may be prepared by distilling a mixture of antimonous sulphate with twice its weight of common salt.

Trichloride of antimony is a volatile, fusible, crystallisable body of a deliquescent nature, and of corrosive properties. It is soluble in hydrochloric acid and in water, but much water will cause a precipitate of an insoluble oxychloride, $SbCl_3$, Sb_2O_3, when added to its solutions.

Antimonous chloride is used in the bronzing of gun barrels, so as to prevent them from rusting.

ANTIMONIC CHLORIDE.

FORMULA $SbCl_5$. MOLECULAR WEIGHT 299·5.

This compound is produced when a current of dry chlorine is passed over or through antimonous chloride, gently heated in a retort. It is a very volatile, slightly yellowish liquid, which emits dense white fumes on exposure to the air, and is decomposed on distillation.

When treated with much water the following reaction occurs: $2SbCl_5 + 7H_2O = H_4Sb_2O_7 + 10HCl$.

With sulphuretted hydrogen, antimonic chloride produces a white crystalline substance of the formula $SbCl_3S$. It also forms interesting compounds with the higher chlorides of phosphorus, selenium, sulphur, etc.

In studies upon so-called organic compounds it is often used as a chlorinating body.

BISMUTH.

Symbol Bi. Atomic Weight 210.

History.—The first distinct mention of this metal is to be found in the last testament of Basil Valentin (fifteenth century), but it is very uncertain whether the term marcasite then applied to this metal, as it occurred naturally, was also at an earlier period used in that sense by Arnold Villanova, Roger Bacon, Albert Magnus, and others, or merely as a designation of any kind of bright mineral. However, bismuth was included by Paracelsus among the semi-metals; Agricola mentioned it as *bisemutum* and *plumbum cinereum*. It was confounded with antimony by Libavius, and with zinc by N. Lemery, and it was not until the year 1739 that the specific characters of this metal were made known by Pott, and afterwards by Bergman.

Occurrence.—Bismuth occurs naturally in the metallic state associated with ores of silver, lead, zinc, nickel, cobalt, etc.; it also occurs, combined with sulphur, as bismuth glance Bi_2S_3; with tellurium as tetradymite Bi_2Te_3; the sulphide also occurs combined with cuprous sulphide as tannenite $Cu_2S.Bi_2S_3$, and wittichenite $3Cu_2S.Bi_2S_3$; with cuprous sulphide and lead sulphide as needle ore $Cu_2S2PbS.Bi_2S_3$, and with nickel sulphide in several minerals; the oxide Bi_2O_3 occurs as bismuth ochre, a silicate as bismuth blende, and the carbonate as bismuthite. The principal source of bismuth is the native metal that occurs in Saxony and Bohemia.

Characters.—Bismuth is a grey coloured metal with a distinct rose tint. It is very brittle and readily crystallisable, and is probably dimorphous, crystallising in forms belonging to both the cubic and hexagonal system. Its density is 9·830 in the solid state, and greater in the liquid state; after being exposed to great pressure, the density of bismuth is reduced to 9·556. Bismuth melts at about 260°, and expands in solidifying; at a higher temperature it volatilises and burns with a bluish-coloured flame, but under ordinary conditions the metal is not readily oxidised by the air. It exhibits the phenomena of diamagnetism in a higher degree than any other substance.

Preparation.—Bismuth is obtained chiefly from the ores containing it in a metallic state, and the method by which it is extracted consists simply in heating the ore sufficiently to melt the metal, so that it separates from the earthy substances and minerals with which it is associated. This process is termed liquation. Sometimes the ore is merely mixed with a little charcoal upon a layer of wood, and after setting fire to the heap at the top, it is allowed to burn downwards; the metal is then picked out of the ashes and remelted, and cast into ingots. A better mode of conducting this operation is to heat the ore in iron tubes fixed in a sloping position in a furnace, as shown in fig. 383. The liquation tubes (*b d*) are about 8 or 12 inches in diameter; the upper ends (*d*) can be closed with sheet-iron covers, and to the lower ends (*b*) are fixed clay or iron plates with small apertures (*o o*), through which the liquid metal runs into the pots (*a a*), which are heated by a small fire at (K) sufficiently to keep the metal liquid, and admit of its being ladled out into moulds. The ore is put into the red-hot tubes at the higher ends (*d*), and after about half an hour, when the metal has run off, the residue is raked out from the higher ends of

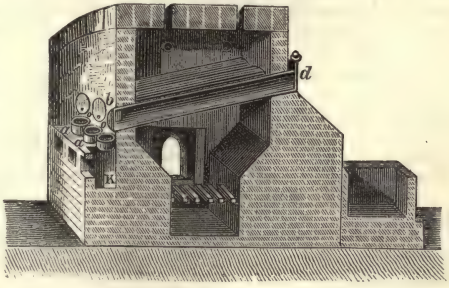


Fig. 383.

the tubes into the water tank beneath. The bismuth thus obtained is impure, containing arsenic, sulphur, lead, copper, etc.; it may be purified by melting it with 10 per cent. of nitre.

The extraction of bismuth from ores of cobalt and nickel is practised in this way at Schneeberg in Saxony, and the residual material is often smelted to obtain the cobalt and nickel in the form of speise, which yields a further quantity of bismuth by liquation. (See COBALT and NICKEL).

Bismuth is also extracted by melting the ore with soda, lime, and fluor spar in crucibles. When the ore contains bismuthous sulphide or arsenical compounds of nickel or cobalt, some metallic iron is added, which combines with the sulphur and arsenic, preventing the formation of speise containing much bismuth; by this means the bismuth is separated from the nickel and cobalt which are obtained as speise, which should not retain more than 2 per cent. of bismuth.

The ores from which nickel and cobalt are extracted at Joachimsthal generally contain some bismuth, and it may be advantageously extracted in this way when it does not amount to more than 2 per cent., provided the ore does not also contain lead, which would be reduced and mixed with the bismuth.

Bismuth is obtained also to some extent as a by-product in the treatment of cobalt ores.

Compounds.—Bismuth forms three series of compounds, in which the metal is respectively divalent, as in the dichloride $BiCl_2$; trivalent, as in bismuthous oxide Bi_2O_3; and pentavalent, as in bismuthic oxide Bi_2O_5. The compounds in which the metal is trivalent are the most stable.

Bismuthous oxide Bi_2O_3 is formed when the metal is heated in contact with atmospheric air, or it may be obtained by heating the basic nitrate to dull redness. It is a pale yellow pulverulent substance that melts at a full red heat and combines readily with silica. It dissolves in strong acids, forming saline compounds. This oxide occurs naturally as bismuth ochre.

Bismuthous hydrate $Bi_2O_3.H_2O$ or $BiHO_2$ is obtained in the form of a white precipitate when a solution of a bismuthous salt is decomposed by an alkali. When heated with excess of potash, the hydrate is converted into bismuthous oxide, which presents the appearance of a yellow crystalline powder.

Bismuthic oxide Bi_2O_5 is a bright red pulverulent substance, obtained by passing chlorine into a concentrated solution of potash containing bismuthous hydrate in suspension, and treating the red-coloured product thus produced with dilute nitric acid. Bismuthic oxide, when heated above 100°, loses part of its oxygen, and thus yields a substance represented by the formula Bi_2O_4, which may be regarded as a saline compound of bismuthic oxide with bismuthous oxide $Bi_2O_5 + Bi_2O_3 = 2Bi_2O_4$. Bismuthic oxide combines with other basic oxides, forming similar compounds, which are called bismuthates.

Bismuth forms two compounds with sulphur: disulphide BiS, a dull black powder obtained in a hydrated state by treating and mixing alkaline solutions of bismuthous oxide and stannous oxide with sulphuretted hydrogen. The trisulphide Bi_2S_3 occurs naturally as bismuth glance; it may be obtained by heating a mixture of powdered bismuth with one-third its weight of sulphur until it melts. This substance expands considerably in solidifying. It is formed also as a brownish-black precipitate by the action of sulphuretted hydrogen on solutions of bismuthous salts.

Bismuthous chloride $BiCl_3$ is a white fusible substance which may be obtained by heating the metal in an atmosphere of chlorine gas; it is very hygroscopic and combines with water, forming a crystallisable hydrate, but is decomposed by a larger proportion of water, forming an oxychloride $BiCl_3.Bi_2O_3$ or BiClO and hydrochloric acid $BiCl_3 + H_2O = BiClO + 2HCl$.

The same substance is formed by mixing solutions of bismuthous nitrate and sodium chloride. Bismuthous chloride combines with the alkaline chlorides, forming crystallisable double salts.

Bismuth dichloride $BiCl_2$ is a brown crystalline substance easily fusible and decomposed by water; it is formed by heating the trichloride with metallic bismuth. At a high temperature it is converted into trichloride and metallic bismuth.

The bromide $BiBr_3$ is a steel grey substance fusible at 200° and resembling fused iodine.

The iodide BiI_3 is a grey crystalline vaporisable substance; when heated in contact with atmospheric air, it forms an oxyiodide BiIO, crystallising in copper-coloured rhombic laminæ.

Bismuth unites readily with other metals, forming alloys which are more easily fusible than bismuth itself. An arsenide containing 3 per cent. of bismuth occurs naturally. Bismuth unites in all proportions with antimony, forming brittle alloys

which expand considerably in solidifying. With tin and lead it forms an alloy known in England as fusible metal, and called in France after its alleged discoverer, métal fusible de d'Arcet. In preparing fusible metal the three constituents are used in varying proportions according to the purpose for which the alloy is required. An alloy consisting of 1 part of bismuth, 2 of tin, and 1 of lead, is sometimes used as a soft solder by pewterers, and in making moulds for toilet soaps. An alloy of 5 parts of bismuth, 2 of tin, and 3 of lead, melts at 93°, and is used for stereotype *clichés*. Another of 8 parts of bismuth, 5 of lead, and 3 of tin, melts at 94°·5, and the alloy, consisting of 2 bismuth, 1 lead, and 1 tin, melts at 94°: all of these are suitable for taking casts of anatomical preparations. A small addition of mercury is said to increase the fusibility. Bismuth and lead in equal parts form a brittle alloy of the same colour as bismuth, and having a density (10·709) greater than the mean of its constituents. With tin bismuth forms an alloy more elastic and sonorous than tin itself, a property sometimes utilised by pewterers. About 4 per cent. of bismuth gives an alloy that is slightly malleable, but with a larger proportion of bismuth to the tin the alloy is brittle. An alloy of tin, bismuth, nickel, and silver is said to prevent iron from rusting.

Uses.—Besides its use alloyed with other metals, as above mentioned, bismuth finds employment in various ways. The property that the pure metal has of regular expansion when heated is utilised in the adjustment of the scale of high-ranged thermometers. The oxide, carbonate, and subnitrate are used in medicine. The subnitrate is known as pearl powder, and is used as a flux for enamels, as a vehicle for the colours of other metallic oxides, and, mixed with fifteen times its weight of gold, in gilding porcelain; it is also used as a cosmetic. A subchloride, too, is used as pearl powder. The nitrate, mixed with a solution of tin and tartar, has been employed as a mordant in calico printing.

BISMUTH NITRATE.

Formula $Bi3NO_3$. Molecular Weight 396.

This salt is obtained by dissolving bismuth in hot nitric acid and evaporating the solution until it crystallises. The crystals are colourless, very deliquescent, and contain five molecules of water. The salt dissolves in dilute nitric acid, but is decomposed by water and converted into a basic salt which forms a white precipitate, and was formerly known as magistery of bismuth. The composition of this precipitate appears to vary according to the extent to which it is washed with water, but approximates to the formula $Bi3NO_3.Bi_2O_33H_2O$.

NICKEL.

Symbol Ni. Atomic Weight 59.

History.—The distinction between this metal and copper was first pointed out in 1754 by Cronstedt, who showed that kupfernickel, the mineral formerly supposed to be a copper ore, and to which the name nickel was derisively applied on account of the failure of all attempts to obtain copper from it, was in reality a compound of a peculiar metal differing in many of its characters from copper.

Occurrence.—Nickel occurs most abundantly as kupfernickel (arsenide or nickel), from which it is extracted, as also from speise, a material which is produced as described, during the manufacture of 'smalt.' Speise may be said to be an impure arsenio-sulphide of nickel.

Kupfernickel is of a pale copper colour, and is found in masses of metallic lustre; it is very brittle and has a specific gravity of 7·3—7·5. Its formula is NiAs, and it is composed of 44 per cent. nickel and 56 per cent. arsenic. Although it is principally obtained from the mines in Saxony, where it occurs associated with the ores of copper, silver and cobalt, considerable quantities have been raised in Great Britian, particularly at Pengelly and St. Austell Consols mines in Cornwall, and at the Bathgate silver mine in Scotland,

An analysis of a foreign kupfernickel made by Rammelsberg shows it to be nearly identical with the English product. Arsenic 48·80 per cent.; nickel 39·94 per cent.; cobalt 0·16 per cent.; antimony 8·00 per cent.; silica 2·00 per cent.

There are various other nickel-bearing minerals, but none of them have any important commercial value, owing to their scarcity. Among these are white nickel ($NiAs_2$) which is found at Reichelsdorf in Hesse Cassel and at Schneeberg in Saxony. Nickel glance (NiAsS) is found in Sweden, in the Hartz, and some parts of Austria; it contains from 20 to 38 per cent. nickel. Antimonial nickel (NiSb) is found at Andreasberg and contains about 29 per cent. nickel. Millerite (sulphide of nickel) occurs in Saxony, Bohemia, Cornwall and South Wales; it contains 64 per cent. nickel. Nickel-linnæite, or siegenite, a mineral containing about 30 per cent. nickel, has been found at La Motte in Missouri. Zaratite, a hydrated carbonate of nickel, also occurs there. Pentlandite (Fe_2NiS_3) is obtained from South Norway, and contains from 18 to 21 per cent. nickel.

The greatest consumption of nickel, as of cobalt, is in England, but for our supplies we are almost entirely dependent upon Norway, the Netherlands, and Northern Germany.

Characters.—Nickel is remarkable for having an atomic weight apparently almost identical with that of cobalt, but it must be admitted that there exists some small doubt about the correctness of the determinations.

Rathoff determined the atomic weight as 59·08; Dumas by the same plan arrived at 59·02; Russell by another method found 58·738; Winkler also by a distinct process found 59·06; R. H. Lee by a study of some organic salts has determined the atomic weight of nickel at 58·00.

Nickel is a bright silver-white, hard but ductile metal, slightly more fusible than iron, which, according to Deville, it surpasses in tenacity. Like cobalt, it is associated with iron in meteorites, and also admits of magnetisation, but it loses this property at a temperature of 330° C. When containing carbon, the metal is more fusible than otherwise. The metal has a sp. gr. of 8·279, but by forging this may be raised to 8·666.

Nickel oxidises in a current of air at a high temperature, and if previously heated will burn in oxygen like iron; the pulverulent metal which results from the reduction by hydrogen of oxide of nickel is, like cobalt when similarly obtained, of a pyrophoric nature.

When suspended in water it is readily attacked by chlorine and bromine, and it is also easily dissolved by nitric acid or aqua regia, but is less soluble in dilute acids.

The oxide of nickel, when strongly heated with charcoal, gives a fusible carbide of the metal.

Preparation.—The principal works in this country for the extraction of nickel are situated near Birmingham, but endeavours are made to maintain the utmost secresy as regards the various processes employed. According to Louyet the method is somewhat as follows:

The speise or native ore, or a mixture of both, is fluxed with chalk and fluorspar in a reverberatory furnace; the slags are thrown away, and the resulting matt is reduced to powder and roasted for twelve hours to free it from arsenic.

The product is next dissolved in hydrochloric acid, and the solution, after separation from what little remains insoluble, is diluted with water; a little bleaching powder is added to peroxidise the iron, and the iron and arsenic are precipitated by neutralisation with milk of lime and boiling. The clear liquor and washings of the precipitate retain all the cobalt and nickel in solution, together with copper, bismuth, and lead. These last three substances are precipitated by means of sulphuretted hydrogen, and the supernatant liquors boiled afterwards to expel the excess of the gas. After this they are again neutralised by milk of lime and more bleaching powder added. Sesquioxide of cobalt is thus obtained, which is washed and ignited, and is then ready for the market, while the nickel still remains behind in the mother liquors, and is obtained therefrom as hydrated protoxide by adding excess of milk of lime.

From the oxide the metal is frequently obtained by a process of cementation. A number of cylinders made of clay are set vertically in a furnace, so that the flame may play on all sides of them. These cylinders are open at the top, and terminate in truncated cones which project beneath the fire bars.

Oxide of nickel, either in lumps or in small cubes, and intimately mixed with charcoal, is introduced at the top, and on the application of a strong heat the metal is reduced, but retains the form of the oxide, and is withdrawn through orifices in the bottoms of the cylinders. As the nickel is withdrawn from below fresh charges of oxide and charcoal are introduced at the top, and so the cylinders are worked on the principle of lime kilns, the process being therefore in a sense continuous.

Sometimes the wet hydrated oxide of nickel is worked into a paste with a small quantity of flour and syrup, giving a mass of a dough-like consistency, which may then be cut up into cubes about $\frac{1}{8}$ of an inch square, and reduced by intense ignition either in crucibles or in tubes, where they are surrounded by charcoal dust.

There are various methods of obtaining the metal in a pure state on the small scale, but as they are nearly all based upon the same principles the description of one will serve to illustrate all.

The roasted ore is dissolved in aqua regia containing an excess of nitric acid, so as to get the iron in a ferric state; excess of ammonia is then added; the ferric oxide is separated by filtration, and caustic potash is added to the blue liquid until the colour has nearly disappeared. In this way a pale green precipitate consisting of hydrated nickel oxide and potash is obtained. On washing with hot water the potash is removed, and the residual precipitate after drying gives, by reduction at a high temperature in a stream of hydrogen, metallic nickel of a pyrophoric nature. On heating in contact with charcoal at a forge a well-fused button of carbide of nickel is obtained.

Nickel oxalate also gives the metal on decomposition by heat, and it may likewise be obtained in laminæ by the electrolysis of a solution of ammonio-nickel sulphate $NiSO_4(NH_4)_2SO_4, 6H_2O$. This method is now often employed where it is desired to deposit nickel in dense layers capable of receiving a good polish.

Uses.—As nickel is now so largely used for coating surfaces of wrought or cast iron, steel, copper, brass, zinc, etc., it is of interest to note the following process which, according to F. Stolba, is very effectual.

A mixture is made of one part of concentrated solution of zinc chloride and two of water, and raised to the boiling point, any turbidity that may exist being corrected by the careful addition of hydrochloric acid. The objects to be nickel-plated are now cleansed and immersed in the zinc solution, and on adding to the latter a little powdered zinc they become lightly coated with it, and to this the nickel will attach itself. Nickel sulphate, or the double salt of potassium and nickel, is now added, either in the dry state or as a solution, until the boiling mixture exhibits a green colour, when a few zinc cuttings are added and the boiling continued. Provided that the liquor remains clear, a closely adhering yellowish nickel deposit occurs, shining or dull, according as the surface on which it is deposited be polished or rough.

The chief use of nickel in the arts is for the preparation of the white alloy known as German silver, more than 600 tons of which are produced annually with a largely increased demand.

Compounds.—Nickel forms two oxides; a protoxide NiO and sesquioxide Ni_2O_3; the latter does not form salts.

The oxide is of an ash grey colour and may be obtained from nickel salts, as the sulphate or chloride, by precipitation with an alkali.

The sesquioxide, which is black, may be obtained by gentle ignition of the nitrate, or by treating the hydrated protoxide with a solution of sodic hypochlorite, when it is precipitated as a hydrate $Ni_2H_6O_6$. On strong ignition it loses part of its oxygen, and on heating it with acid it forms proto-salts.

Nickelous chloride NiCl is obtained by dissolving the oxide in hydrochloric acid; the resulting solution, on evaporation, yields crystals of a green hydrated character, containing $9H_2O$.

In the anhydrous state (obtained on heating) it forms a yellowish-brown mass which volatilises at higher temperatures in crystalline scales that are but slowly soluble in water.

When heated in a current of air some oxide is found. Three sulphides of nickel are known, of the formulæ Ni_2S, NiS, and NiS_2.

The protosulphide (NiS) occurs, as we have already seen, in a native state (millerite) in grey or yellowish crystals soluble in nitric acid. These may be artificially produced by fusing sulphur with nickel. When a salt of nickel in solution is precipitated by ammonic hydric sulphide, a black hydrate of this sulphide is produced.

The subsulphide (Ni_2S) is yielded by heating nickel sulphate in contact with charcoal or hydrogen.

The disulphide (NiS_2) is obtained as a steel grey powder, when a mixture of carbonate of nickel, potassic carbonate and sulphur is heated to redness and treated with water.

Several double sulphates of nickel and other metals are known, the most important of which is the compound potassic salt $NiSO_4,K_2SO_4,6H_2O$, which may be obtained in a crystallised form. Nitrate of nickel $Ni2NO_3$, $6H_2O$ crystallises in emerald green prisms which are readily soluble in water; the solution on heating yields a basic salt.

Several carbonates are known, all of which have a green colour. On pouring the nitrate of nickel into an excess of solution of sodic bicarbonate, the normal carbonate of nickel is thrown down as a crystalline powder.

All salts of nickel give in the oxidising flame of the blowpipe, with borax, a reddish-yellow glass which pales as it cools.

Various alloys of nickel are known. Argentane, or German silver, consists ordinarily of 8 parts of copper, 2 of nickel, and 3 of zinc, but owing to its yellow tint it is not employed for the better purposes. White argentane or plate has one part more nickel than German silver, and is a very fine alloy. Electrum has yet one more part nickel than argentane plate and resists oxidation almost perfectly.

If the proportion of nickel be increased much beyond that in which it exists in electrum, the alloy is hard and difficult to work.

Packfong is also a compound of zinc, nickel, and copper, in which the proportions of the constituent metals may vary considerably. According to Miller, a good alloy is obtained by using 51 parts of copper, 30·6 of zinc and 18·4 of nickel.

Futenang is the Chinese name for a similar alloy, composed of 8 parts of copper, 6½ of zinc, and 3 of nickel. In consideration of the increased price of nickel experienced during the last few years, it is reasonable to expect that before long processes will be devised for extracting the 3 or 4 per cent. of nickel contained in the nickeliferous pyrites that occur in Italy and elsewhere. These pyrites might first of all be employed in the manufacture of sulphuric acid and then submitted to processes for extracting nickel, just as now the silver is extracted from the burnt residuum.

The following analyses of various alloys are by A. Röpler:—

	White Copper	Paris Alloy	Chinese Packfong		Used for knife handles	Used for forks
Copper . . .	88·00	65·9	43·8	40·4	55·0	50·0
Nickel . . .	8·75	16·8	15·6	31·6	20·0	25·0
Zinc	—	13·0	40·6	25·4	25·0	25·0
Iron	1·75	3·4	—	2·6	—	—

NICKEL OXIDE.

FORMULA NiO. MOLECULAR WEIGHT 75.

This substance has a specific gravity of 5·75, and is obtained in the anhydrous form by ignition of the nitrate or carbonate in a covered crucible. As precipitated from its salts by alkalies it is a light green bulky hydrate (NiH_2O_2?) and may be obtained in a crystalline form by decomposing the solution of nickel carbonate in ammonia by ebullition.

This oxide of nickel has a curious power of combination with potash or soda, yielding insoluble compounds which require very great and continued washing with hot water to entirely decompose them. The potash or soda may be replaced by other bases, as baryta, strontia, etc.

NICKELOUS SULPHATE.

FORMULA $NiSO_4$. MOLECULAR WEIGHT 155.

This salt crystallises in rhombic prisms of a green colour, containing seven molecules of water, and requiring three parts of cold water for solution; it is insoluble in alcohol. It may be obtained by dissolving the metal, or its oxide or carbonate, in sulphuric acid. By crystallisation at a temperature of 15°—25° C. octahedra are obtained containing only $6H_2O$ (sp. gr. = 2·037).

COBALT.

Symbol Co. Atomic Weight 59·8.

History.—The elemental character of cobalt was originally recognised by Brandt, in 1733, although it had been known for some considerable time previous that the mineral named kobalt was capable of imparting a blue tint to glass.

This mineral was well known to the Bohemian and Saxon miners of the fourteenth century, but at that time was without use.

Brandt first detected the metal in certain ores of a bismuthic character, and since his investigation other chemists have studied this metal and its compounds; among them Bergman, Tassaert, Thenard, and Proust.

Occurrence.—Excepting traces of the metal which occur in meteoric iron, cobalt is not found in the native state. It occurs in nature usually in association with arsenic as speis-cobalt ($CoAs_2$) and occasionally with arsenic and sulphur as cobalt glance (CoSAs). Its ores are as a rule very complicated, and contain nickel, iron, bismuth, copper, and sometimes manganese.

Smaltine (arsenical cobalt or tin-white cobalt) occurs largely at Schneeberg in Saxony, at Joachimsthal in Bohemia, and at Wittichen, Siegen, Saalfeld, and at Mansfeld. It is also found in various parts of Cornwall. This mineral contains from 20 to 23 per cent. of cobalt, but some of this is replaced in some samples by varying quantities of iron, nickel, and copper.

It is, however, from cobalt glance or cobaltine that most of the cobalt preparations are made. It is found largely in Sweden and Norway, sometimes occurring in very definite crystals of the cubic system. From its yellowish-white colour tinged with red this mineral is sometimes known as bright white cobalt; it contains from 33 to 44 per cent. cobalt, 43 to 55 per cent. arsenic, ½ to 20 per cent. sulphur, together with a varying percentage of iron. The black oxide has been met with in the Western States of America associated with the sulphide and other oxides. Cobalt also occurs as erythrite or cobalt bloom $Co_3As_2O_8,8H_2O$, often found side by side with cobaltine. Pyrolusite and mispickel sometimes contain as much as 5 per cent. cobalt, and it also enters into the composition of skutterudite (Co_2As_3).

The ores of cobalt are found chiefly in the primitive rocks, either as imbedded crystals or finely dispersed, and from this fact and the varying nature of the other associated matters the value of the ores varies extremely.

Characters.—Cobalt is nearly as infusible as iron, and cannot be reduced from its oxides by carbon without assimilating some of the latter into its constitution, thus giving a product not unlike cast iron. The metal has a dull grey colour shaded by red. Its specific gravity is, according to Berzelius, 8·513; but Lampadius has assigned to it the specific gravity 8·7 and Turner 7·834. It possesses a specific heat 0·10696 (Regnault). The purest metal is obtained by ignition of the oxalate (CoC_2O_4), when carbonic anhydride is evolved; thus $CoC_2O_4 = Co + 2CO_2$. The metal may also be obtained from its oxide by reduction with hydrogen; but as obtained in this manner it takes fire on exposure to the air, producing cobaltoso-cobaltic oxide. Like iron, it is attracted by the magnet, but loses this property by gentle heating. When the metal is heated to redness it absorbs oxygen, forming first of all a blue oxide, which, if time be allowed, peroxidises into black Co_2O_3 or Co_3O_4 according to the temperature employed. The mineral acids dissolve it slowly, even when aided by heat, hydrogen being evolved, and the respective salts resulting. These latter impart to their solutions a fine red colour.

Preparation.—As cobalt is never used in the arts, its metallurgy is confined to laboratory processes which all start with the oxide obtained as hereafter to be described. The oxide is dissolved in nitric acid, the resulting solution is then neutralised, and nitrite of potassium added, when a yellow precipitate is formed. This is washed, dissolved in acid, and the cobalt precipitated either as oxide by means of an alkali, or as oxalate by ammonic oxalate. In either case the product is dried, mixed with oil, and

strongly heated in a well-luted charcoal-lined crucible, when a button of the carbide of cobalt is obtained.

To obtain chemically pure cobalt, it is best to employ purpureo-cobaltic chloride (a compound ammonium salt), which on ignition gives cobaltic chloride, a substance admitting of easy reduction by hydrogen at a red heat.

Uses.—Although metallic cobalt is not used in the arts, a blue pigment containing it and known as smalt is largely consumed, and is prepared by fusing properly prepared cobalt ore with certain materials to form a suitable glass.

Manufacture of Smalt.—The arsenical cobalt ores which are mainly used in preparing smalt first undergo a process of sorting, powdering, and washing. If bismuth be present, it has to be removed before the stamping operation by a process of liquation in iron tubes. The ores are next roasted in a current of air, the object being to oxidise the cobalt, whilst the nickel, copper, and iron remain in combination with arsenic and sulphur. Some of the arsenic is converted in this way into arsenious acid, and proper arrangements are made for condensing this substance in a chamber known as the poison gallery. This roasting process is not carried to perfection, otherwise all the metals would be oxidised, and by entering into the composition of the smalt would impair the colour, and thus exercise a depreciative influence on its value.

From 4 to 5 parts of the roasted product or schlich, as it is called, are next mixed with 10 parts of ground calcined quartz and 4 parts of potassic carbonate, together with white arsenic as obtained in the poison galleries above alluded to. This mixture is then submitted to fusion in pots arranged in a furnace like that in an ordinary glass-making factory. The pots are a little conical, being about 18 inches in diameter at the top, and 14 at the bottom, with a thickness of 2 inches. Each pot holds about 84 lbs. of the mixture and its normal period of duration is about seven or eight months. In this fusion operation the oxide of cobalt combines with the fused potassic silicate, forming a deep blue glass, while the mixed metallic arsenides and sulphides fuse and collect at the bottom of the pots, forming when cold a brittle mass of metallic appearance and termed speise. It is cast into ingots, and is used in the manufacture of nickel. The blue glass is from time to time ladled out and poured into cold water, by which operation it is reduced to innumerable fragments, and these are afterwards powdered and then ground between granite stones so constructed that the grinding takes place under water, which carries off with it the smalt thus obtained in a finely divided state. The washings so obtained are made to pass through a number of tanks arranged so that the liquor overflows from one to the other successively, and in this way a number of deposits are obtained, of which the earlier ones are the coarsest in grain, and the later ones the finest in division. The greater the degree of subdivision, the less intense is the colour.

After drying, the azure is broken up by mallets, and is then reduced again to fine powder by falling from a hopper upon two wooden cylinders turning horizontally. In the next stage of its manufacture it is further dried upon shelves at a temperature of about 105° to 112° F., after which it is returned to the braying machine. Finally it is sifted and packed. The yield of marketable blue as produced from the blue glass is about 3 tons of azure for 5 tons of glass. The two following analyses of smalt are by Ludwig:—

	Norwegian	German Smalt	
		High Eschel	Coarse Eschel
Silica	70·86	66·20	72·11
Oxide of cobalt	6·49	6·75	1·95
Potash and soda	21·41	16·31	20·04
Alumina	·43	8·64	1·80
Ferric oxide	·24	1·36	1·40

Smalt is chiefly manufactured in Saxony, but it is also made in Norway, Silesia, and Hesse. The furnaces employed are built universally upon the same principles, but in certain details there is a difference according as the fuel employed is wood or coal, etc.

Smalt is employed in fresco-painting, and in the manufacture of porcelain pottery, stained glass, etc.

The paper manufacturers used it for a purpose similar to that which leads to its use in washing—namely, to correct the yellow colour which often exists in animal-sized papers. The important feature regarding smalt is that only those

reagents which attack glass have any action upon it; hence it constitutes a more stable colour than most blues.

Zaffre of commerce is a very crude oxide of cobalt, prepared by roasting cobalt ore and mixing the product with several times its weight of silicious sand.

Thenard's blue is another valuable pigment containing cobalt in the state of oxide, and it may be said to consist of alumina coloured by oxide or phosphate of cobalt. There are several modes of preparation, the most approved of which is as follows:—Cobaltous nitrate is precipitated by hydric disodic phosphate and the precipitate so obtained is mixed whilst moist with hydrated alumina produced by adding carbonate of soda to a solution of alum free from iron. The moisture is dried and ignited in a well-covered crucible, but notwithstanding this care, the gases produced by the fuel exercise an injurious influence on the colour, to correct which a little oxide of mercury is usually added to the mass, so that it is constantly in contact with an oxidising atmosphere, by reason of the oxygen thus generated. The mercury which is formed simultaneously volatilises and so does no harm.

In another process a mixed solution of cobalt sulphate and ammonia alum is evaporated to dryness, and the residue subjected to intense ignition in a furnace.

Cæruleum is the name of a blue pigment made by Messrs. Rowney and Co. It has the following composition: binoxide of tin, 49·66 per cent.; oxide of cobalt, 18·66 per cent.; silica and lime sulphate, 31·68 per cent.

This pigment like Thenard's blue is used both as an oil and water colour.

Rinman's green consists of oxide of zinc coloured with oxide of cobalt, and is prepared by precipitating a mixture of zinc sulphate and cobalt sulphate with sodic carbonate and igniting the precipitate after due washing. Or it may be made from the two nitrates, or from nitrate of cobalt and oxide of zinc mixed, by simple evaporation and ignition.

Printer's blue is used for printing patterns on china, and is made by fritting silicate of cobalt with nitre, after the addition of a little basic sulphate. To use it, it must be mixed with oil, printed on paper and transferred to the biscuit ware; it is during the process of glazing that the colour is developed.

Other colours are prepared from cobalt, but they do not call for special mention.

Compounds.—Cobalt is divalent, and forms two classes of salts corresponding to the two classes of iron salts, ferrous and ferric.

The cobaltous salts are the more stable, the more numerous, and the most important. They all are red in a state of solution, but are blue when anhydrous, and all are decomposed at a moderate red heat, with the exception of the sulphate.

The similarity between the oxides and salts of cobalt and those of iron is seen from the following formulæ:—

Cobaltous oxide .	CoO	Cobaltic oxide .	Co_2O_3
Ferrous „ . .	FeO	Ferric „ .	Fe_2O_3
Cobaltous chloride .	$CoCl_2$	Cobaltic chloride .	Co_2Cl_6
„ nitrate .	$Co2NO_3$	„ nitrate .	Co_26NO_3
„ sulphate .	$CoSO_4$	„ sulphate .	Co_23SO_4

The salts derived from cobaltous oxide may be prepared by disolving the oxide in the respective acids.

The chloride is also prepared by passing chlorine over metallic cobalt; at a high temperature it volatilises. It may be obtained by crystallisation in a ruby red form containing $6H_2O$, and its aqueous solution, when mixed with excess of hydrochloric acid, gives a blue solution, becoming pink on dilution. This solution in a dilute state may be used as a sympathetic ink; the characters formed by writing it are invisible when cold, but become blue on warming, owing probably to the production of the anhydrous salt, because the colour gradually disappears again when the paper is exposed to hygroscopic moisture. The colour can, moreover, be modified at desire; the addition of a small amount of an iron or nickel salt gives the writing a green colour; a salt of zinc produces in like manner a red colour, and one of copper gives a yellow tint.

Three sulphides of cobalt are known—viz. protosulphide CoS; sesquisulphide Co_2S_3; and a disulphide CoS_2. The first of these is the most important, and is obtained in a hydrated condition by precipitating cobaltous acetate with sulphuretted hydrogen. Cobaltous sulphide quickly oxidises and passes into sulphate.

There are known also a number of ammoniacal compounds of cobalt of scientific interest only.

All compounds of cobalt are easily recognisable by reason of the intense blue colour which they impart to a bead of borax before the blow-pipe.

The alloys of cobalt are unimportant. The metal unites by fusion with antimony

and arsenic, and the formation of the alloy is attended by incandescence; the resulting alloys have an iron grey colour and are very brittle.

COBALTOUS OXIDE.

FORMULA CoO. MOLECULAR WEIGHT 75·8.

In order to prepare oxide of cobalt from the speise or matt which forms in the roasting of arsenical ores of cobalt, it is dissolved in strong hydrochloric acid, and iron and arsenic are precipitated by the addition of milk of lime. The supernatant liquors are run off after settling, and submitted to a current of sulphuretted hydrogen so long as metallic sulphides are formed. The clear liquor resulting after settling is again drawn off, and now on adding a solution of bleaching powder, cobaltous oxide is precipitated in a hydrated condition, and the product, on being heated to redness, gives the blue oxide of commerce; when heated further to whiteness, there is obtained the prepared oxide of commerce.

The manufacture of these oxides is carried on by the nickel refiners at Birmingham; the products are used in the potteries and by glass makers and enamellers, either alone or with various fluxes, for giving a blue colour to their wares.

Pure protoxide of cobalt when dried at a low temperature is greenish grey, and on ignition to dull redness in a current of air it gives an oxide Co_3O_4, corresponding to the magnetic oxide of iron Fe_3O_4.

COBALTIC OXIDE.

FORMULA Co_2O_3. MOLECULAR WEIGHT 166.

This substance may be prepared in several ways, one of the best methods being as follows. The hydrated protoxide of cobalt is suspended in water and submitted to a current of chlorine; in this way cobaltous chloride is formed and dissolved, whilst black hydrated cobaltic oxide is precipitated; thus:—

$$3CoH_2O_2 + Cl_2 = Co_2H_6O_6 + CoCl_2.$$

If, in this reaction, an alkaline solution be substituted for the water, then all the cobalt is obtained as peroxide.

A gentle heat renders this oxide anhydrous; at higher temperatures it is converted into a black oxide Co_3O_4. This cobaltoso-cobaltic oxide, as it is called, corresponds to the compounds termed manganites which are obtained by blowing air through protoxide of manganese held in suspension, in the presence of lime. In this way, in fact, in Weldon's process of manganese regeneration, there is obtained, among other bodies, one whose presumable formula is MnO, MnO_2—that is, a manganite of manganese, in which the protoxide seems to exist as a basic radicle and towards which the peroxide acts as a combining acid radicle.

Cobaltoso-cobaltic oxide CoO, Co_2O_3, would appear to be a similar substance, and may be obtained in steel-grey octahedra by boiling a solution of roseo-cobaltic chloride. This last named substance is one of the ammonium combinations of cobalt previously referred to, and has the composition (Co_2Cl_6, $10NH_3$, H_2O). Cobaltic oxide Co_2O_3 has feeble basic powers; in its hydrated form it is soluble in cold acids, but the salts so produced become quickly reduced into those of the protoxide, even at normal temperatures; the acetate is the most stable salt.

COBALTOUS NITRATE.

FORMULA $Co2NO_3$. MOLECULAR WEIGHT 183·8.

This salt crystallises with 6 molecules of water, and is perhaps the most important salt of cobalt. It is made by dissolving cobaltous oxide in nitric acid, and as a salt is of a deliquescent character.

When a concentrated solution of this salt is acidified with nitric or acetic acid, and mixed with one of potassic nitrite, a beautiful yellow salt is precipitated in a crystalline form. It contains 13·6 per cent. of cobalt, and has the formula Co_2O_3, $2N_2O_3$, $6KNO_3$, $2H_2O$ (A. Stromeyer).

MANGANESE.

Symbol Mn. Atomic Weight 55.

History.—This metal was first isolated by Gahn in 1774, and although the black oxide or dioxide occurring naturally had long been known and used for decolorising glass, the existence in it of a peculiar metal was not recognised. Originally the mineral known as brownstone and consisting essentially of manganese dioxide was regarded as an iron ore; but various researches about the years 1770 to 1774 proved that the metal contained in this mineral is distinct from iron.

Occurrence.—Manganese exists somewhat abundantly in nature, chiefly occurring in an oxidised state. The dioxide occurs as pyrolusite or grey manganese ore, which has a metallic lustre, and a specific gravity of 4·85; this is the most abundant ore and, from its uses in various manufactures, the most important. It is largely consumed for the generation of chlorine in the manufacture of bleaching powder, of which more than 100,000 tons are made annually in Great Britain. Pyrolusite contains about 63·3 per cent. manganese and 36·7 per cent. oxygen. Large quantities are found in Spain, Devonshire, and Cornwall. Braunite is the native form of the sesquioxide, and contains 69·68 per cent. manganese and 30·32 per cent. oxygen. Hausmannite, which is a rarer ore, consists of a mixture of protoxide and sesquioxide. Manganite is a hydrated sesquioxide, and manganese blende consists of manganous sulphide. As carbonate manganese occurs in diallogite, and as hydrosilicate in rhodonite. Wad or bog manganese, which is a hydrated peroxide, occurs largely in Cornwall, Devonshire, the Hartz, and Piedmont. When mixed with linseed oil it forms a mass which is liable to inflame spontaneously.

The ores used in commerce contain from 60 to 75 per cent. of peroxide of manganese, and are chiefly derived from Spain, Germany, France, Belgium, and Holland.

Characters.—Manganese is of a greyish-white colour and is brittle; when obtained by Brunner's process it is hard enough to scratch steel, but it has been questioned whether this property is not due to the presence of silicon derived from the materials employed. Manganese is feebly magnetic, and oxidises on exposure to the atmosphere. It decomposes water at normal temperatures, and to preserve it, it is necessary to place it in sealed tubes or under naphtha. When the metal is strongly heated in contact with carbon and silicon, it combines with these substances; a silicuretted carbide is thus produced.

Preparation.—The metal is extracted from its compounds only with considerable difficulty. One of the best methods is to mix the carbonate into a paste with oil and sugar or oil and lampblack, and to expose the mixture, contained in a crucible lined with charcoal and provided with a cover luted on, to the heat of a smith's forge. In this way after about two hours a metallic button results, which contains however a little carbon.

The metal may also be obtained, according to Brunner, by imitating the process of Deville for the reduction of aluminum. The chloride or fluoride treated with metallic sodium under these conditions gives metallic manganese.

When a solution of chloride of manganese is subjected to electrolysis plates of the reduced metal are obtained.

It may be obtained in a pulverulent form by heating its amalgam in a tube which is filled with the vapour of rock oil (Giles).

Uses.—The metal has no uses in the arts in a pure state, but an alloy of manganese with iron is largely used in the manufacture of steel and Bessemer metal.

Compounds.—Manganese, like many other metals, cannot well be classed according to its atomicity or quantivalence, because this power is a fluctuating quantity which varies with the compounds, in some of which it is divalent, in others trivalent or heptavalent.

With oxygen it forms a number of compounds, four of which are well defined; the

other two have an existence known only in combination. The protoxide MnO is a powerful base; the sesquioxide Mn_2O_3 has feebly basic powers; the red oxide Mn_3O_4 and the black dioxide MnO_2 have no basic characters.

The potassium salts of the two higher oxides are potassic manganate K_2MnO_4, supposed to contain MnO_3, and potassic permanganate $K_2Mn_2O_8$, supposed to contain Mn_2O_7.

The dioxide would seem to possess powers of combination of an acid character, according to Mr. Weldon's interpretation of the results he has obtained in the peroxidation of manganous oxide by air in the presence of an excess of lime. He claims to have demonstrated the existence of various compounds, which he terms manganites and sesquimanganites; thus $CaOMnO_2$ and $CaO2MnO_2$ are obtained, a small portion of the CaO being usually replaced by an equivalent amount of MnO.

Of the chlorides, manganous chloride $MnCl_2$ is the most important; a trichloride Mn_2Cl_6 or manganic chloride is also known. Besides these, it is said a tetrachloride $MnCl_4$ and yet another chloride $MnCl_7$ also exist. Manganic chloride is obtained when the sesquioxide is treated with cold hydrochloric acid; heat converts it into manganous chloride and free chlorine. The tetrachloride is obtained in ethereal solution by passing hydrochloric acid gas into a properly cooled mixture of manganese dioxide and ether; it imparts to the ether a fine green colour. The heptachloride $MnCl_7$ is said to be formed when potassic permanganate is dissolved in strong sulphuric acid and fused sodic chloride is gradually added; under these conditions a greenish-yellow gas is obtained which condenses to a liquid at 0°. Water decomposes it into permanganic acid and hydrochloric acid; and Dumas regards it as a heptachloride. H. Rose, however, believes it to be an oxychloride $MnCl_2O_2$ analogous to chromic oxychloride. It is said that fluorides corresponding to the above described chlorides have been formed.

Manganese forms two sulphates, viz., manganous sulphate $MnSO_45H_2O$ and manganic sulphate, which is a deep green powder that combines with potassic sulphate, giving a double salt crystallising in octahedra of the composition $K_2Mn_2"4SO_4$.

Sulphide of manganese is obtained in a hydrated state as a reddish-yellow precipitate $MnS + H_2O$, when a manganous salt is precipitated by sulphydrate of ammonium.

The carbonate $MnCO_3$ frequently accompanies spathic iron; as a white hydrate $2MnCO_3.H_2O$, it is formed by precipitating a salt of manganese by an alkaline carbonate. The carbonate is decomposed on heating, leaving an oxide.

An arsenide and a bromide are also known.

Manganese yields several alloys, none of which however are of much importance. They are difficult to prepare, because it is difficult to reduce metallic manganese. Mr. F. F. Allen directs as follows for preparing the copper alloy: a mixture of dioxide or carbonate of manganese is fused with cupric oxide and charcoal in a plumbago crucible at the highest attainable temperature. Alloys with tin, lead, etc., have also been prepared. Manganese in combination with iron gives a harder and more elastic metal than is iron alone.

MANGANOUS OXIDE.

Formula MnO. Molecular Weight 71.

In an anhydrous condition this oxide is obtained by ignition of the carbonate or any higher oxide in a current of hydrogen. It is a green coloured powder liable to oxidise in the air, and when ignited in contact with air combustion takes place and a brown oxide results.

This oxide is soluble in acids, and forms the corresponding salts from whose solutions alkalies reprecipitate the oxide as a pinkish hydrate MnH_2O_2, which rapidly absorbs oxygen from the air or oxygen gas and passes into the sesquioxide Mn_2O_3.

MANGANIC OXIDE.

Formula Mn_2O_3. Molecular Weight 158.

Occurs naturally as braunite and as a hydrate in manganite $Mn_2O_3.H_2O$. It may be prepared as stated above from the protoxide or from the carbonate by suspension in water and passing chlorine gas through the mixture. If excess of chlorine be used the dioxide results. It forms also the principal part of the residue left behind when the dioxide is heated for the purpose of making oxygen.

This oxide has a brown colour, and is resolved by strong nitric acid into monoxide and dioxide, the former of which alone dissolves. Heated with strong sulphuric acids, oxygen is liberated, and manganous sulphate results. With hydrochloric acid it forms

chlorine gas. On strong ignition it loses one-eighth of its oxygen, and leaves the red oxide Mn_3O_4.

The colour of the amethyst is supposed to be due to the presence of this oxide.

MANGANOSO-MANGANIC OXIDE.

Formula Mn_3O_4. Molecular Weight 229.

This oxide corresponds to the magnetic oxide of iron. It occurs naturally as hausmannite, and is obtained when any one of the other oxides is heated strongly in the air. It is incapable of forming definite salts, although it is dissolved both by phosphoric and sulphuric acids.

BINOXIDE OF MANGANESE.

Formula MnO_2. Molecular Weight 87.

The native forms of this oxide are found both massive and crystallised. It is a good conductor of electricity, being strongly electro-negative in the voltaic circuit.

It may be prepared by precipitating a salt of manganese by a solution of bleaching powder, or by gentle ignition of nitrate of manganese.

It is black in colour, and does not form corresponding salts with acids.

On ignition it yields one-third of its oxygen, and leaves the red oxide $3MnO_2 = Mn_3O_4 + O_2$. Treated with sulphuric acid the following reaction occurs:

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

With hydrochloric acid it gives rise to chlorine:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

It is by this process that chlorine is manufactured for the preparation of bleaching powder; the chloride of manganese which results is precipitated by an excess of milk of lime, and air is then blown through the mixture.

In this way (Weldon's process) the manganese is again peroxidised, giving rise to the compounds treated of above, and these on treatment with fresh hydrochloric acid yield a further supply of chlorine, while the manganese may be continually regenerated.

When manganate or permanganate of potassium is decomposed by an acid, hydrated dioxide is precipitated, MnO_2H_2O, as a reddish-brown body.

Another hydrate, $4MnO_2H_2O$, is obtained on heating the red oxide of manganese with nitric acid.

According to Fremy, manganic dioxide not only acts as an acid, but also as a base, forming definite salts with acids—for example, a sulphate of the formula MnO_2SO_3.

The manganese of commerce is never pure manganese peroxide, but always contains, besides lower oxides of manganese, a number of other admixtures which reduce its value. Since it is the peroxide of manganese which yields chlorine with hydrochloric acid, the value of commercial manganese to the chlorine producer depends upon the percentage of manganese peroxide it contains. In order to determine the amount of peroxide in a sample of manganese, a weighed quantity of the manganese is treated with an excess of hydrochloric acid, so as to liberate all the chlorine it is capable of yielding. This chlorine is absorbed in a dilute solution of caustic soda, and then determined by titration.

For this purpose 4·35 grms. of finely powdered commercial manganese is weighed and placed in a glass flask, with from 15 to 20 c.c. of concentrated hydrochloric acid. The flask is then closed as quickly as possible with an india-rubber cork, in order to avoid escape of chlorine, a glass tube bent at an angle of 45° passing through a perforation in the cork. The end of this glass tube is fastened into the neck of an inverted retort reaching as far as the bulb of the retort. The retort is filled to about four-fifths with a solution of caustic soda, so that no air is contained in the bulb itself. The glass flask containing the manganese and hydrochloric acid is then gently heated, the chlorine evolved being immediately absorbed by the caustic soda in the retort. The temperature is eventually raised to the boiling point and kept at this point until chlorine ceases to be evolved, which is ascertained from the peculiar noise caused by the condensation of pure hydrochloric acid. All chlorine having been driven out of the glass flask, this is disconnected from the retort, and the contents of the retort are poured into a litre flask, the retort being washed with water and the washings added to the contents of the litre flask, which is then filled with water up to the mark. The

litre flask is then shaken up and the chlorine contents of the liquid (10 c.c. being taken at a time) determined by titration, either according to the method of Gay Lussac or Penot and Mohr.

Since the equivalent weight of peroxide of manganese is 87, and 4·35 grms. of manganese is taken, a pure sample ought to yield 3·5 grms. of chlorine, and accordingly 10 c.c. of the Gay Lussac arsenious acid solution ought to be saturated by 10 cc. of the chlorine solution prepared as above. If, however, less chlorine has been evolved, more of the chlorine solution is required. If, for instance, 14 c.c. be required to completely oxidise 10 c.c. of the Gay Lussac arsenious acid solution, the amount of manganese peroxide contained in the sample of commercial manganese would be according to the proportion:

$$14 : 10 = 100 : x$$
$$x = 71{\cdot}43$$

The manganese sample would therefore accordingly contain 71·43 per cent. of active manganese peroxide.

Instead of absorbing the chlorine by means of a dilute solution of caustic soda, it may be passed into a weighed quantity of Penot's solution of sodium arsenite, the non-oxidised arsenious acid being titrated back by means of iodine and starch paste.

Determination of the quantity of hydrochloric acid required for the complete decomposition of a given quantity of manganese.—The value of manganese is not alone dependent upon the quantity of chlorine it is capable of yielding with hydrochloric acid, but also upon the quantity of hydrochloric acid required for its complete decomposition. Pure manganese peroxide liberates half the chlorine contained in a given quantity of hydrochloric acid; but commercial manganese contains, besides manganese peroxide, compounds which decompose hydrochloric acid, setting very little, if any, chlorine free. Manganese oxide, for instance, decomposes hydrochloric acid according to the equation:

$$Mn_2O_3 + 6HCl = 2MnCl_2 + 3H_2O + 2Cl.$$

Thus it liberates only one-third of the chlorine contained in hydrochloric acid. Manganous oxide yields no chlorine when treated with hydrochlori acid

$$MnO + 2HCl = Mn\,Cl_2 + H_2O,$$

thus using up hydrochloric acid in a manner no way suitable to the chlorine manufacturer. Besides these oxides, commercial manganese may contain substances which consume hydrochloric acid without evolving chlorine, as, for instance, iron oxides, etc.

But the most objectionable admixtures in commercial manganese are the carbonates, such as calcium and barium carbonates, which consume hydrochloric acid and liberate carbonic acid instead of chlorine. This carbonic acid is a great nuisance in the chlorine chambers where bleaching powder is being prepared, as it combines with part of the lime to form calcium carbonate, which resists the action of chlorine. This causes not only a loss of hydrochloric acid, but also waste of lime at the same time.

According to Fresenius the quantity of hydrochloric acid required for the complete decomposition of a definite quantity of manganese may be determined in the following way.

The amount of acid in a strong solution of hydrochloric acid (spec. grav. 1·10) is determined by titration either with ammoniacal copper oxide or with normal potash solution. 10 c.c. of this acid is placed in a small flask containing the manganese to be examined, which must be in a finely powdered state. The flask is then closed with a perforated caoutchouc cork fitted with a glass tube 3 feet long, then gradually heated until all the chlorine has been expelled. The flask and its contents are allowed to cool, diluted with water, and the quantity of free acid again determined either by titration with ammoniacal copper oxide or with normal potash solution.

MANGANATES.

When an oxide of manganese is fused with caustic potash, oxygen is absorbed from the air, and a dark green mass results containing manganate of potassium K_2MnO_4. Potassic nitrate or chlorate, if added during the fusion, assists the oxidation. If soda be used instead of potash, the sodium salt is obtained, and a solution of either yields crystals by evaporation in a vacuum. This is necessary because the salts readily absorb more oxygen passing into permanganate.

Barium manganate $BaMnO_4$ may be similarly prepared.

PERMANGANATES.

Permanganates are obtained when manganates are dissolved in much water; manganese dioxide is precipitated in a hydrated state, and the solution becomes purple from the formation of a permanganate:

$$3K_2MnO_4 + 2H_2O = MnO_2 + K_2Mn_2O_8 + 4KHO.$$

This effect is accelerated by heat, but retarded by the presence of much free alkali. Potassic permanganate may be readily made by heating to dull redness a mixture prepared by drying a solution of five parts caustic potash containing in mixture $3\frac{1}{2}$ parts of potassic chlorate and 4 parts of finely divided manganese dioxide. After an hour's heating, the mass is cooled, powdered, neutralised with sulphuric acid, filtered, and evaporated. On cooling, beautiful acicular crystals of potassic permanganate result.

Or the salt may be obtained by passing a current of carbonic anhydride through potassic manganate in solution:

$$3K_2MnO_4 + 2CO_2 = K_2Mn_2O_8 + 2K_2CO_3 + MnO_2;$$

or chlorine may be used instead—thus:

$$2K_2MnO_4 + Cl_2 = K_2Mn_2O_8 + 2KCl$$

Other permanganates are well known, such for instance as the argentic salt, which is also crystalline.

Both the manganates and the permanganates are powerful oxidising agents.

Permanganic acid $H_2Mn_2O_8$ is prepared by dissolving the potassium salt in sulphuric acid diluted with one molecule of water and distilling the mixture at 60°–70°. The acid then passes over in violet vapours, which condense to a greenish-black liquid which has a powerful attraction for water, and is so powerful in its oxidising effects as to instantly set fire to paper or alcohol.

MANGANOUS CHLORIDE.

Formula $MnCl_2$. Molecular Weight 126.

As already explained, this salt is obtained on a large scale in the manufacture of chlorine. It crystallises in plates of a delicate pink colour containing 4 molecules of water. These when heated yield the anhydrous salt which is soluble in alcohol, and forms a double combination which may be obtained in a crystalline form; it has the formula $MnCl_2,4C_2H_6O$.

MANGANOUS SULPHATE.

Formula $MnSO_4$. Molecular Weight 151.

This salt is used to some extent by calico-printers. It is a very soluble rose-coloured salt, isomorphous with magnesium sulphate. On the large scale it is prepared by heating manganese dioxide and coal in a closed vessel, and dissolving the crude protoxide thus obtained in sulphuric acid, with addition of a little hydrochloric acid. The solution is then evaporated to dryness and the residue exposed to a red heat, by which any ferric sulphate which is present is decomposed. From the product so resulting water dissolves out pure sulphate of manganese. It is used by the printers by steeping the cloths in it, and then passing them through a solution of bleaching powder which precipitates the insoluble hydrated dioxide within the fibres of the articles, thus producing a permanent brown. Sulphate of manganese crystallises either with 7 or 5 molecules of water, and forms double salts with the sulphates of the alkali metals; thus the potassium double salt is $MnSO_4,K_2SO_4,6H_2O$.

When sulphate of manganese is crystallised from boiling sulphuric acid, it forms an acid salt of the formula MnH_2SO_4.

CHROMIUM.

Symbol Cr. Atomic Weight 52·5.

History.—Chromium was discovered in 1797 by Vauquelin, in a mineral having the composition of plumbic chromate $PbCrO_4$. This, however, occurs but rarely in nature.

Occurrence.—Chromium is not found very abundantly in nature, and it never occurs in the metallic state. The only ore which is found in any abundance is chrome iron ore, a compound of oxides of chromium and oxides of iron, corresponding to magnetic oxide of iron (FeO, Cr_2O_3 or $FeCr_2O_4$). Chrome iron ore occurs chiefly in serpentine, which is found in Saxony, Silesia, Bohemia, Transylvania, in Norway, the Ural and various parts of North America. It is found in a massive state in the Shetland Isles, while the chief supply is derived from Sweden and North America. Chromium is also found as sesquioxide (chrome ochre), and as already mentioned in the form of chromate of lead, a crystalline mineral of great beauty.

Characters.—In the hard crystalline state the metal resists the action of strong acids, even nitro-hydrochloric acid; otherwise it is readily attacked by dilute hydrochloric acid, less so by dilute sulphuric acid, and even less by strong nitric acid.

When heated to redness in the air, it tarnishes, and is gradually covered with a thin film of green oxide. When thrown into a flame fed with oxygen, it scintillates like iron, and when melted with potassic chlorate it burns very brightly. It also exhibits a brilliant incandescence when heated in chlorine gas; it also combines with bromine, iodine, fluorine, cyanogen, nitrogen, oxygen, phosphorus, and sulphur. When absolutely pure, it is less fusible than platinum.

Preparation.—There are several processes for the preparation of metallic chromium. Deville obtained it by reducing chromium sesquioxide in a lime crucible, by means of charcoal at a high temperature; it is thus obtained as a porous mass consisting of grains as hard as corundum and of specific gravity 5·9. Wöhler prepared metallic chromium by reducing the sesquichloride by means of zinc at a red heat. The regulus of zinc obtained in this way is heated with dilute nitric acid, which dissolves the zinc and leaves the chromium as a grey powder. Peligot obtained it in a similar form by the use of potassium in the place of zinc, and Fremy, by employing the vapour of sodium along with a current of hydrogen, produced metallic chromium in hard shining crystals.

Chromium is also obtained in brittle laminæ when a solution of the sesquioxide is submitted to electrolysis (Bunsen).

Compounds.—Chromium forms two classes of salts, viz. the chromous and chromic compounds. In the first of these the chromium is bivalent like iron in ferrous chloride; as for instance in the chloride $CrCl_2$ or the oxide CrO, etc. In the chromic compounds the metal behaves as a triad or tetrad, and the salts are comparable to those of ferric iron, as the oxide Cr_2O_3 and the chloride Cr_2Cl_6, etc. There is a third oxide CrO_3 which combines with water and basic oxides forming a series of compounds called chromates. The hydrate or hydrogen salt is chromic acid H_2CrO_4; this acid is analogous to sulphuric acid.

Chromous oxide CrO is known only in the hydrated state, and is obtained when chromous chloride $CrCl_2$ is precipitated by caustic potash; in this state it is brown and absorbs oxygen rapidly; it even decomposes water with avidity, setting free hydrogen, and forming an intermediate oxide of chromium CrO,Cr_2O_3,H_2O. Chromous oxide forms salts which are of a pale blue colour and have a great affinity for oxygen; it forms a double sulphate with potassic sulphate $Cr''K_2\dot{2}SO_4$. The sesquioxide Cr_2O_3 corresponds to ferric oxide. The dioxide (CrO_2) is obtained as a brown substance by digesting chromic oxide with excess of chromic acid, or by partial reduction of chromic acid; it may be a chromic chromate Cr_2O_3,CrO_3.

Perchromic acid is the name given to the blue solution obtained when chromic acid or a solution of potassic dichromate acidulated with sulphuric acid is treated

with dilute peroxide of hydrogen; it has been suggested that the colouring principle may have the formula $H_2Cr_2O_8$, containing an oxide Cr_2O_7 analogous to permanganic acid.

Chromium forms two chlorides, $CrCl_2$ and Cr_2Cl_6; the latter of these will be described more fully hereafter. Chromous chloride may be obtained by reduction of chromic chloride at a red heat in a current of hydrogen; the white product dissolves easily in water, giving a blue solution liable to undergo atmospheric oxidation and capable of absorbing nitric oxide just as ferrous chloride does. By atmospheric oxidation a solution of chromous chloride turns green and yields chromic oxychloride Cr_2Cl_6,Cr_2O_3.

With ammonic sulphide, chromous chloride gives a black precipitate of chromous sulphide.

Two fluorides of chromium are well known, the trifluoride Cr_2F_6 and the hexfluoride CrF_6. The former of these is obtained by treating dry sesquioxide of chromium with hydrofluoric acid, and strongly heating the dried mass. The trifluoride, which is dark green, sublimes at a high temperature and crystallises in regular octahedra. The hexfluoride is produced on distillation of a mixture of 4 parts plumbic chromate with 3 of powdered fluor spar and 8 of concentrated sulphuric acid:

$$PbCrO_4 + 3CaF_2 + 4H_2SO_4 = PbSO_4 + 3CaSO_4 + 4H_2O + CrF_6.$$

The deep red vapours of hexfluoride which pass over may be condensed to a red liquid by use of a very low temperature. On contact with water the substance is decomposed, yielding hydrofluoric acid and chromic acid:

$$CrF_6 + 3H_2O = CrO_3 + 6HF.$$

It is said an intermediate fluoride between these two which have been described can be obtained by the action of hydrofluoric acid on the brown dioxide of chromium.

Chromium also unites with bromine, iodine, cyanogen, phosphorus, and sulphur; besides the chromous sulphide above referred to, there is a chromic sulphide Cr_2S_3, which may be obtained in black scales when the vapour of carbon bisulphide is passed over strongly heated chromic oxide contained in a porcelain tube. By addition of sulphide of ammonium to the solution of a chromic salt, hydrated sesquioxide is precipitated and sulphuretted hydrogen set free.

A nitride of chromium Cr_3N_4? has been described by Schrotter.

Chromic nitrate Cr_26NO_3 is a soluble salt of a green colour; on gentle ignition it yields brown dioxide of chromium CrO_2 or Cr_2O_3,CrO_3.

Chromic oxalate forms two well-defined series of double salts of the general formula: $M_6'Cr_2'''6C_2O_4$ and $M_2'Cr_2'' 4C_2O_4$.

Little is known of the alloys of chromium; it combines with aluminum and iron, and also forms an amalgam which is obtained on treating a solution of chromic chloride with sodium amalgam; the product, when heated in a current of hydrogen, leaves metallic chromium as a pulverulent sponge.

CHROMIC OXIDE.

FORMULA Cr_2O_3. MOLECULAR WEIGHT 153.

This oxide in an anhydrous condition may be variously prepared.

(*a*) In dark green crystals when the vapour of chromic oxydichloride is passed through a red-hot porcelain tube—$4CrCl_2O_2 = 2Cr_2O_3 + 4Cl_2 + O_2$.

(*b*) By heating ammonic or potassic dichromate.

When required for industrial purposes it is obtained:

(*c*) By mixing solutions of mercurous nitrate and potassium chromate or dichromate, and exposing the precipitated mercurous chromate to a red heat. The sesquioxide so obtained as a residue is of a fine green colour, and, like alumina which has been strongly heated, is insoluble in acids.

(*d*) Another good method of preparation consists in strongly igniting in a covered crucible a mixture of 4 parts of potassic chromate in powder with 1 part of starch; potassic carbonate is thus formed, and may be dissolved out from the residue, and the chromic oxide remaining only requires a second calcination to obtain it in a clear bright green form.

Chromic oxide is not decomposed by heat, and it is therefore used in enamel painting.

The pink colour used on earthenware is prepared by heating to redness a mixture of 30 parts of stannic oxide, 10 of chalk, and 1 of potassic chromate: the product is finely powdered and washed with weak hydrochloric acid. A beautiful rose tint is thus obtained (Müller).

The crystalline sesquioxide is used in the preparation of razor strops.

The hydrated oxide may be obtained by boiling potassic dichromate in the presence of alcohol or sulphurous anhydride, when potassic chromate is formed; and on addition of ammonia, the sesquioxide is thrown down as a greyish-green hydrate. This bulky form of the hydrated oxide retains alkali with pertinacity; it dissolves readily in acids, and forms salts of a green colour, which do not crystallise.

Chromic oxide forms another set of salts having a violet colour which admit of crystallisation, and the oxide which ammonia precipitates from their solutions is of a bluish-green colour.

Berzelius accounted for these results by admitting the existence of two distinct hydrates of chromic oxide. Through the researches of Fremy and Siewert these hydrates have been more particularly made known. According to the conditions of preparation and drying, the amount of water associated with the oxide is determined. The following combinations exist:

Cr_2O_3, $9H_2O$; Cr_2O_3, $7H_2O$; Cr_2O_3, $6H_2O$; Cr_2O_3, $4H_2O$; and Cr_2O_3, H_2O.

The hydrated sesquioxide parts with its water below redness, and if heated beyond this point it becomes incandescent, shrinks, and is then insoluble in acids. Chromic oxide is a weak base, resembling ferric oxide and alumina; its salts are green or purple.

CHROMIUM TRIOXIDE.

Formula CrO_3. Molecular Weight 100·5.

This compound may be readily obtained by mixing 4 measures of concentrated cold solution of potassic dichromate with 5 of oil of vitriol; on cooling, the chromic trioxide crystallises out in beautiful crimson needles. Chromic anhydride is very soluble in water; but, although soluble in dilute and even more concentrated acid than that of 1·55 sp. gr., it is not soluble except to a slight extent in acid of that particular strength.

To rid the crystals of sulphuric acid, they should be first drained on a tile, then dissolved in water and precipitated by an equivalent amount of acid barium chromate, BaH_2 $2CrO_4$, calculated upon the sulphuric acid present. On evaporation of the resulting solution in vacuo, the chromic anhydride is obtained pure.

Chromic trioxide may be also obtained by decomposing chromium hexafluoride with a little water. It is deliquescent and easily freed from water by drying at a gentle heat. It is black when hot, but regains its dark red colour on cooling; it fuses at 200°C, and at a higher temperature evolves oxygen while the sesquioxide is left behind. When heated with hydrochloric acid, chlorine is liberated according to the following reaction:

$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + 3Cl_2.$$

Chromic trioxide combines with sulphuric acid to form several crystalline compounds, which are all decomposable by water.

When in contact with water, for which the trioxide of chromium exhibits a strong affinity, it exists as chromic acid, H_2CrO_4, which is bibasic, and corresponds to sulphuric acid.

Chromic acid forms three classes of salts, namely, basic, normal, and acid; the normal salts have a yellow, and the acid salts an orange colour.

Potassium chromate, K_2CrO_4, is made by calcination of chrome iron ore with nitre or with potassium carbonate, or with caustic potash.

This operation is ordinarily conducted in a reverberatory furnace, using the chrome iron ore in a powdered condition. The furnace product is lixiviated with water, and the solution on evaporation yields crystals of the chromate in an anhydrous condition.

Potassium dichromate, $K_2Cr_2O_7$, is obtained by heating chrome iron ore to redness and plunging it into cold water, by which means it is rendered friable. It is finely powdered and heated to bright redness with a mixture of chalk and potassium carbonate in a reverberatory furnace with frequent stirring in a current of air. Any calcium chromate that may have formed is afterwards decomposed by lixiviating the product with water, and addition if necessary of potassium carbonate. In any case the yellow solution is drawn off, supersaturated with nitric acid, and, after separation by filtration of any silica that may thus be precipitated, evaporated, when crystals of potassium dichromate are obtained, and may be purified by recrystallisation. The chalk is used in the furnace operation to keep the mass in a porous state, which is one favourable to the oxidation.

This salt may also be obtained by treating the neutral salt with a calculated quantity of sulphuric acid.

Potassium dichromate melts when heated, and is soluble in 10 parts of water.

By treating potassium dichromate with an equivalent of such bases as lime or magnesia several double salts may be obtained. Thus we have magnesio-potassium chromate, $K_2Mg2CrO_4.2H_2O$, which crystallises in oblique rhombic prisms.

Mitscherlich obtained a trichromate of potassium, $K_2Cr_3O_{10}$, by acting on the dichromate with excess of nitric acid; and Siewert, by evaporating a solution of this compound in nitric acid, obtained a tetrachromate $K_2Cr_4O_{13}$.

Sodium chromate may be similarly prepared, using soda in the place of potash; it crystallises with $10H_2O$. An acid sodium chromate, $2NaHCrO_4.H_2O$, can also be obtained in ruby coloured crystals.

Argentic chromate, Ag_2CrO_4, is precipitated when solutions of silver nitrate and potassic chromate are mixed; it is a reddish-brown powder, soluble in hot dilute nitric acid, and crystallising therefrom on cooling in ruby-red crystals.

Chromate of calcium is soluble, while the chromates of barium, zinc, and mercury are insoluble.

Plumbic chromate is the only other compound that calls for notice here; it is largely used in organic analysis by reason of the facility with which it yields oxygen to organic matter heated in contact with it, while it fixes any such bodies as chlorine or iodine which may be present in the substance to be analysed or 'burned.'

Plumbic chromate is the basis of the pigment known as chrome yellow, and is obtained by precipitating a solution of acetate of lead with one of potassium chromate or dichromate.

At 200–250°C it becomes brown, and at a much higher temperature it fuses and evolves about 4 per cent. of oxygen, basic plumbic chromate being formed.

$$8PbCrO_4 = 4PbCrO_4PbO + 2Cr_2O_3 + 3O_2.$$

A dibasic plumbic chromate is also known of the formula $(2PbO,CrO_3)$; it is used to impart a permanent orange to calico, and may be obtained by fusing one part of the normal plumbic chromate with 5 parts of nitre. Potassium chromate and the dibasic plumbic chromate are thus produced, while the potassium salt may be dissolved out from the product by means of water.

CHROMIC SULPHATE.

Formula $Cr_2 3SO_4$. Molecular Weight 393.

This salt is obtained by dissolving the hydrated sesquioxide in dilute sulphuric acid. It forms with the sulphates of the alkalies double combinations which are highly crystalline; important among these is the ammonium compound:

$$CrNH_4 2SO_4 12H_2O.$$

There are three varieties of chromic sulphate, represented as follows:

Red insoluble sulphate	$Cr_2 3SO_4$
Green soluble sulphate	$Cr_2 3SO_4, 5H_2O$
Violet „ „	$Cr_2 3SO_4, 15H_2O$.

CHROMIC CHLORIDE.

Formula Cr_2Cl_6. Molecular Weight 318.

This compound may be obtained in the anhydrous condition by passing a current of dry chlorine gas over an intimate mixture of chromium sesquioxide and charcoal heated to redness in a porcelain tube. The chloride which forms sublimes and deposits in the cool part of the tube in crystalline plates of a violet colour.

The crystals are quite insoluble in cold water; but, when boiled, a green solution is formed containing a trace of the dichloride. This change from the violet insoluble condition to the green soluble variety is attended with evolution of heat.

The crystals of chloride above described are also not attacked by sulphuric, hydrochloric, or even nitro-hydrochloric acid.

The green hydrated chromic chloride is readily formed by dissolving chromic hydrate in hydrochloric acid, or by boiling the chromates of lead or silver, or chromic acid with hydrochloric acid in the presence of a reducing agent such as alcohol or sulphurous acid.

$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + Cl_6.$$

On evaporation of the solution a green syrup results; and this, heated to 100°C. in a current of dry air, yields a mass containing $Cr_2Cl_6,9H_2O$; in a vacuum the solution yields Cr_2Cl_6,H_2O.

A compound of chromic chloride and chromic oxide known as chlorochromic oxide CrO_2Cl_2 is formed when equal parts of potassium dichromate and common salt are distilled with one and a half times their combined weight of sulphuric acid; this compound passes over as a dark red vapour which condenses into a liquid like bromine. Or 10 parts of common salt may be previously fused with 17 parts of potassic chromate; the mass is then broken into small fragments and heated in a retort, with 30 parts of oil of vitriol.

Water decomposes chlorochromic oxide into hydrochloric and chromic acids, just as it similarly decomposes chloromolybdic, chlorotungstic, and chlorosulphuric oxides.

When chlorochromic oxide is dropped into strong ammonia it solidifies with incandescence, and it sets fire to alcohol, owing to the intense heat evolved in the reaction.

If heated to 180–190° C., it is resolved into a dark-coloured, deliquescent powder, trichromyl dichloride, $Cr_2Cl_2O_6$ or $3CrO_2Cl_2$, which takes fire when gently heated in hydrogen gas, being resolved into chromium sesquioxide, hydrochloric acid, and water.

$$2Cr_2Cl_2O_6 + 10H = 3Cr_2O_3 + 4HCl + 3H_2O.$$

GOLD.

Symbol Au. Atomic Weight 197.

History.—Gold has been known from the earliest times on record, and has always been regarded as the king of metals by reason of the properties which qualify it for the uses to which it is applied. The estimation in which the alchemists regarded this metal is shown by the continuous vain endeavours they made to transform the baser metals into gold.

Occurrence.—Gold is most widely distributed in nature, and occurs chiefly in the metallic state, sometimes crystallised in cubes, associated with quartz, iron oxide, etc. It occurs in the crystalline rocks, the trachytic and trap rocks, and alluvial deposits. The larger masses of filiform, arborescent shapes are known as *pepitas* or *nuggets*. The gold dust of commerce is obtained from the sands of various rivers, and is separated by a simple process of washing. Although gold occurs in many parts of the world, being found for instance in small quantity in the pyritic formations of Wicklow in Ireland and in Cornwall, also in Hungary and Transylvania, in Piedmont, Spain, China, Japan and other countries, yet the large supplies are now derived from California and Australia, while the new gold field of British Columbia is also very productive. Formerly Brazil, Hungary, and the Ural mountains furnished the chief supply.

Native gold is generally associated with silver in a greater or less degree, and the percentage of gold contained in the native alloy, although sometimes as low as 28 per cent., is usually from 88 to 98 per cent. Thus Californian gold averages from 87·5 to 88·5 per cent., and Australian from 96 to 96·6 per cent. gold. In certain kinds of iron pyrites the amount of gold is but a few dwts. per ton, nevertheless processes have been devised for the profitable extraction of even these small quantities.

Recently, E. Sonstadt has demonstrated the presence of minute traces of gold in sea water.

Characters.—Gold is of a fine yellow colour and metallic lustre; it is soft and surpasses all other heavy metals in malleability, the thinnest gold leaf being of no greater thickness than $\frac{1}{200000}$ of an inch. In ductility it ranks next to silver and admits of drawing into wire.

The density of the metal is 19·5, and it fuses according to Becquerel at 1037°C.

Gold is one of the best conductors of heat and electricity, and suffers no change by exposure to the air and water; neither is it attacked by the unmixed acids, but it dissolves readily in aqua regia.

Extraction.—Gold is obtained by two distinct processes termed *placer mining* and *vein mining*, both of which consist essentially in the separation of the metal by mechanical means from the earthy substances with which it is associated.

Placer mining.—This process is applied to the metal found in strata of clay, sand and gravel; it is as follows. Into a pan made of stiff tin plate or sheet iron, having a flat bottom of about 12 in. in diameter, and whose sides are from 5 to 6 in. high, sloping outwards at an angle of 45°, is charged the 'pay dirt,' as it is termed, so as to three fourths fill the pan. The pan is then immersed in about a foot depth of water, and the miner by working the contents with his hands and shaking from time to time removes the clay as a kind of thin mud; the light sand follows the clay, while the stones and pebbles rest on the top of the finer and denser gold sand, and are removed by the hands. Finally there remains only gold dust and a certain small quantity of black magnetic iron-sand, to get rid of which the dust is dried and then placed in a 'blower' or shallow tin scoop open at one end; into this the miner blows, shaking the scoop from time to time, and he thus removes the black iron-sand which is carried away in the current of air. The 'cradle,' 'tom' and 'puddling box' are the names which have been given to other pieces of apparatus designed and used for the same purposes as the pan just described. The 'sluice' is the form of washing apparatus now usually employed in California, and consists virtually of a long wooden trough,

through which a stream of water constantly flows; it is further provided with suitable arrangements for preventing the gold dust from being carried away mechanically. The gold remains behind in the apparatus employed, or it is caught and amalgamated with mercury.

Vein mining.—The quartz bearing gold is finely powdered and is then placed on the rough surface of blankets or skins, over which a current of water flows; the gold is caught in this way, or it is amalgamated with mercury. The most usual method of arresting very fine gold is to amalgamate the surface of a copper plate, and to allow the water containing gold dust to flow over it.

From the amalgamated gold the excess of mercury is removed by filtration through a prepared skin, and what remains in the skin is then subjected to distillation in a cast-iron retort. The gold so obtained is usually submitted to fusion, for the purpose of being cast into ingots. Dr. Wurtz and Mr. Crookes have both patented the use of a little metallic sodium with the mercury used for amalgamation processes, and it is said to be beneficial in some cases, especially where the gold is at all of a greasy nature.

In the case of poor ores of gold, containing sulphide of copper and iron, etc., these are first allowed to disintegrate and oxidise by atmospheric influences or are washed, before they are submitted to the amalgamation process. Gold which has been treated by amalgamation ordinarily contains nothing but silver, which may be removed by nitric acid, if the proportion of silver be about 66 per cent. of the alloy; if it be below this, by being protected by the gold it fails to dissolve in the nitric acid. In such cases, therefore, the gold must first be alloyed into the necessary amount of silver, a process known as *quartation*.

Gold containing silver and copper may also be refined by boiling repeatedly with concentrated sulphuric acid; sulphates of silver and copper are thus formed, and sulphurous anhydride generated. From the sulphuric acid solution, the silver may be regained by precipitation with copper.

Refining of Alloys containing little Gold.—The alloy is melted, granulated, and treated with sulphuric acid in the way above described; the residual gold, still containing silver and some copper, is melted and treated in the manner described above for alloys containing a large amount of gold.

From the solutions of silver sulphate obtained in refining operations, silver is precipitated by hanging strips of copper in the warm diluted solution, the silver powder being finally melted together.

Parting by Quartation.—This method consists in forming an alloy of 1 part gold and 2 parts silver, granulating it, treating and boiling the granulated alloy with pure nitric acid of sp. gr. 1·345 for five hours, in stoneware pots placed in a water bath, the whole being frequently stirred. The undissolved gold is allowed to settle during the night, the liquid is drawn off, and the treatment with nitric acid repeated in the same way as before. The liquid from the second operation contains very little silver, and is used for a further quantity of the alloy. The liquid from the first treatment is treated with sodium chloride, to separate the silver as chloride. The gold, after being washed, is pressed, dried and melted.

The separation of gold and silver by means of aqua regia is very seldom practised. It depends upon the fact that, when alloys of the two metals are treated with aqua regia, both are converted into chlorides, and the gold chloride being soluble in water, can be readily separated from the insoluble silver chloride.

It is, however, only with alloys containing very little silver that this method can be adopted, because the silver chloride forms a coating upon the pieces of alloy, and prevents the further action of aqua regia.

Pure gold may be obtained from any alloy containing it, by solution in nitro-hydrochloric acid; separation of any chloride of silver by filtration; evaporation till all acid is expelled; solution of the residue in water acidulated with hydrochloric acid and precipitation with ferrous sulphate:

$$6FeSO_4 + 2AuCl_3 = 2(Fe_2(SO_4)_3) + Fe_2Cl_6 + Au_2$$

Metallic gold is thus obtained as a fine brown powder, which when suspended in water and viewed by transmitted light is of a purple colour. Silver and some other metals when present may be removed from gold by a process introduced by F. B. Miller, and now used in the Royal Mint. This consists in forcing a current of chlorine gas through the melted metal; argentic chloride thus forms and collects upon the surface, whilst any chlorides of arsenic, antimony, bismuth and zinc that may result from the presence of these metals, are volatilised.

Compounds.—Gold forms two series of compounds, termed respectively the *aurous* and *auric*; in the first of these it is univalent, and in the latter it is trivalent.

LIBRARY OF THE

Gold forms two oxides Au_2O and Au_2O_3, and two chlorides AuCl and $AuCl_3$; auric bromide $AuBr_3$ is also known, and two iodides corresponding to the chlorides. There are also two sulphides Au_4S_4 and Au_2S_3. Hydrated auric oxide combines with the alkalies forming salts termed aurates.

When dilute gold solutions are treated with stannous chloride a brownish purple precipitate known as 'purple of Cassius' is formed. It is this compound which is employed to colour the red glass of Bohemia, and for enamel painting. The composition of the precipitate is not exactly known, but after ignition it consists of a mixture of stannic oxide and metallic gold. Oxalic acid slowly reduces gold solutions to the metallic state.

The alloys of gold are interesting and numerous. The most useful one is that which it forms with copper; it is of a redder colour than pure gold, harder, and more fusible, but not so ductile nor so malleable.

British standard gold contains 8·33 per cent. of copper, and has a specific gravity of 17·157. The standard gold of France and the United States contains 10 per cent. of copper.

Silver unites with gold in all proportions; giving an alloy which is nearly white when the two medals are in equal proportions.

Palladium communicates also a white colour to gold, but renders it brittle.

The electrum mentioned by Pliny was an alloy of gold and silver, containing, according to Klaproth, 66·7 per cent. gold or 2 gold to 1 silver. A native amalgam of gold Au_2Hg_3 is found in small yellowish crystals, having a specific gravity of 15·47, in the native mercury of Mauposa in California.

T. H. Henry obtained also a solid amalgam which crystallised in shining four-sided prisms of great lustre, and which was not decomposed by boiling nitric acid; its formula proved to be Au_8Hg.

Uses.—In its finely divided state, gold is used for gilding porcelain articles. These are first painted with an adhesive varnish, and after partially drying are brushed over with a mixture of the powdered metal with some fusible enamel. The articles are next fired and the gilt portions subsequently burnished.

The fine ruby colour possessed by Bohemian red glass is due to the presence of gold. Of course the great use of gold is in the coinage of the world, while it is also largely used in the fabrication of ornamental articles.

Gilding upon wood-work, etc., is effected by the use of gold-leaf, while the gilding of metals is brought about by the use of aurous potassic cyanide AuCyKCy, or of aurous potassic sulphide AuKS, as in the operations of electro-silvering.

Gilding on copper may be performed by immersion of the articles in a solution of mercuric nitrate, and then shaking them with a soft lump of gold amalgamated with mercury; in this way the articles are covered with a film of the amalgam from which the mercury may be expelled by heating.

AUROUS OXIDE.

Formula Au_2O. Molecular Weight 409·2.

This compound is obtained as a dark green powder by adding a dilute solution of potash to one of aurous chloride. It is slightly soluble in excess of the alkali; while digestion with ammonia transforms it into fulminating gold. Hydrochloric acid converts aurous oxide into metallic gold and auric chloride.

AURIC OXIDE.

Formula Au_2O_3. Molecular Weight 441·2.

This oxide is best prepared, by adding magnesia to a solution of auric chloride, which gives sparingly soluble aurate of magnesium; or digesting this with nitric acid, magnesia is removed and the teroxide of gold is left as an insoluble reddish-yellow powder. If the nitric acid employed be weak, the yellow hydrate Au_2O_3, $3H_2O$ is obtained, but if strong acid be taken then the anhydrous brown powder results. It is reduced both by heat and by exposure to light; at 245°C it is resolved into gold and free oxygen. Although soluble in nitric, sulphuric, and hydrofluoric acids, no true salts are formed, because on dilution with water the teroxide is re-precipitated. It is also soluble in hydrochloric, hydrobromic, and hydriodic acids, forming auric trichloride, tribromide, and triodide.

Hydrated auric oxide is soluble in the alkalies, forming salts which are termed

aurates, the solutions of which are yellow, and may be used for electro-gilding purposes.

Potassic aurate ($KAuO_2$, $3H_2O$) crystallises in yellow needles, and a compound of this with acid sulphite of potassium, or potassium aurosulphite, is also known, $2(KAuO_2, 4KHSO_3).H_2O$. Both sodio-aurous thiosulphite and bario-aurous thiosulphite are known salts ($Na_3Au(S_2O_3)_2.2H_2O$) and $Ba_3Au_2(S_2O_3)_4$.

AUROUS CHLORIDE.

Formula AuCl. Molecular Weight 232·1.

Aurous chloride is obtained as a yellowish white mass insoluble in water, when the trichloride is kept for some time at a temperature of about 175°C; under these conditions free chlorine is generated.

Even in the cold, and more quickly when hot, water decomposes this substance into the trichloride and metallic gold. At about 200°C aurous chloride gives up its chlorine.

AURIC CHLORIDE.

Formula $AuCl_3$. Molecular Weight 303·1.

This is by far the most important compound of gold, and is formed, as already stated, when gold is dissolved in nitro-hydrochloric acid. By evaporating the solution at a low temperature, the chloride is obtained as a dark red deliquescent mass. It is also formed as a sublimate when gold leaf is heated to 300°C in a current of chlorine.

Auric chloride is soluble in water, alcohol, and ether, and combines with a number of metallic chlorides, forming double salts termed chloro-aurates.

Thus, there are known the following salts among others; the sodium salt NaCl, $AuCl_3$, $2H_2O$; the potassium salt $2(KCl, AuCl_3)$, $5H_2O$; and the ammonium salt NH_4Cl, $AuCl_3$, H_2O.

Like platinic chloride, it also combines with the chlorides of organic bases and alkaloids, but from the ease with which auric chloride is reduced, its use cannot be recommended so strongly for these purposes.

PLATINUM.

Symbol Pt. Atomic Weight 197·1.

History.—Platinum was first recognised as a distinct metal, by an assayer in Jamaica, named Wood, who pointed out its characteristics in 1741.

According to another account, the metal was discovered in the auriferous sand of the river Pinto in the district of Choco in South America, by a Spanish traveller named Ulloa; it derives its name from the Spanish word 'Platina' (meaning '*little silver*').

Occurrence.—Platinum always occurs in the native state in rounded or flattened grains of a metallic lustre, which contain, besides platinum, the following other metals: palladium, rhodium, ruthenium, and iridium.

More rarely it occurs in nodules alloyed with gold, and traces of silver, and with copper, iron and lead.

The deposits of platinum are met with chiefly in valleys traversing serpentine, and everywhere it is associated with the débris of the earlier volcanic formations. It is rarely that the grains of native ore exceed the size of peas, but now and then masses are found weighing sometimes as much as twenty pounds.

Platinum is found chiefly in Mexico, Brazil, and the Ural Mountains, besides which sources it has been met with in California and Australia.

The largest quantity of platinum at present produced comes from the Ural districts, and is worked from the auriferous sands of Kuschwa, Nischne, Tagilsk, and Goroblagodat.

Thirty-five cwts. of the metal are annually afforded by Russia, and this is said to be five times the total amount given by Brazil, Borneo, St. Domingo, and the States of Columbia.

The native grains have usually a grey colour, like that of tarnished steel, the cavities being filled with earthy or ferruginous material, and sometimes grains of the magnetic oxide of iron. The specific gravity of these native grains varies from 15 to 18·94, which latter figure relates to the larger specimen of M. Humboldt which weighed more than 2 ounces avoirdupois.

The native ore contains from 73 to about 86 per cent. of platinum; the following analyses are by Deville and Debray.

	Columbia		California		Russia	Oregon
Platinum	86.20	76·82	85·50	76·50	77·50	51·45
Indium	0·85	1.18	1·05	0·85	1·45	0·40
Rhodium	1·40	1·22	1·00	1·95	2·80	0·65
Palladium	0·50	1·14	0·60	1·30	0·85	0·15
Gold	1·00	1·22	0·80	1·20	Little	0·85
Copper	0·60	0·88	1·40	1·25	2·15	2·15
Iron	7·80	7·43	6·75	6·10	9·60	4·30
Osmiridium	0·95	7·98	1·10	7·55	2·35	37·30
Sand	0·95	2·41	2·95	1·50	1·00	3·00
Lead	—	—	—	0·55	—	—
Osmium and loss	—	—	—	1·25	2·30	—
	100·25	100·28	101·15	100·00	100·00	100·25

Platinum has only been known in Europe since 1748, and was at first introduced into the market as 'white gold.'

Characters.—Platinum is a very white metal of great ductility and malleability, besides which it is the heaviest metal known, having a density of about 21·50; in hardness it is about equal to copper.

Deville and Debray state that platinum, like silver, has the power of absorbing oxygen when melted, and, if in considerable masses, spits on rapidly cooling.

In the state of very fine wire the metal may be melted in an ordinary blowpipe flame; otherwise the heat of the oxyhydrogen flame is required to fuse it.

Among the acids aqua regia alone attacks it, while the alkalies and their carbonates have an action upon it only at elevated temperatures,

Under the influence of heat it expands very little, and is inferior to gold, and ranks very near to iron, in its conductivity of heat and electricity.

When heated with phosphorus, the two elements readily combine; sulphur has very much less attraction for it, and chlorine no action upon it.

Platinum has a remarkable capacity of inducing combination of gases which may be presented to it; this power is exhibited in a faint degree by bright surfaces of the metal, but much more strongly by spongy platinum, which is obtained on strong ignition of ammonio-platinic chloride. Platinum black has a still greater power of the same kind. It may be variously prepared; as, for instance, by reduction of platinic chloride solution by sodic carbonate and sugar on boiling, or by dissolving platinum chloride in hot caustic potash and adding alcohol gradually to the mixture.

Platinum in this state is like lamp black in appearance, and readily absorbs oxygen. The power of finely divided platinum to cause the combination of hydrogen and oxygen has been ascribed to the power of the metal to absorb and condense into more intimate contact the respective gases.

Finely divided platinum is also useful in effecting the decomposition of hydrochloric acid by air or oxygen, when these gases are passed over it at a red heat, thus obtaining water and chlorine.

Preparation.—When gold is present in sufficient quantity, the platinum is first subjected to a process of amalgamation in order to remove it, after which the ore is generally treated by a method devised by Wollaston.

The method may be described as follows:—

After removing the gold, the ore is extracted first with nitric acid, and afterwards with hydrochloric acid in order to free it from the more oxidisable metals. It is then placed in carboys or stoneware vessels heated on a sand bath, and connected with suitable means for condensing the acid vapours generated in the next stage of the extraction. This consists in extracting the ore with aqua regia, always keeping the hydrochloric acid in excess. When the solution of the ore is completed, the liquors are run off from the insoluble osmiridium, and foreign earthy matters allowed to settle, and the supernatant solution fully precipitated with solution of sal-ammoniac, NH_4Cl. This operation requires about 41 parts of the salt to 100 of ore, and the salt for use is dissolved in 5 times its weight of water. The precipitate obtained in this way is the double salt $2NH_4Cl, PtCl_4$, which is but sparingly soluble.

The mother liquors, yet containing a considerable amount of platinum, are precipitated by bars of zinc or iron; this operation gives a black deposit containing platinum, and this, on re-solution in aqua regia and precipitation with ammonic chloride, gives a further quantity of the double salt.

The compound chloride is then heated to redness in black-lead crucibles, by which means the ammonia and chlorine are expelled and metallic platinum left.

The spongy platinum is then rubbed between the hands and mixed with water intimately, and by a process of levigation, the lighter non-metallic impurities are carried away; the metal then remaining usually retains a little iridium. While in the form of a dense mud, it is poured into a gun metal or brass cylinder somewhat conical in form and well fitted with a steel piston, and, after ramming with a wooden piston, the whole mass is subjected to strong pressure by means of the steel piston.

The discs of metal obtained in this way, and having a specific gravity of about 10, are next exposed to a strong white heat in a wind furnace, and the ingot forged by hammering until rendered homogeneous, and the specific gravity is about 21·5.

When a metal of greater purity is required, a modification of the process just described is employed.

When the aqua regia solution is boiled, chlorine is evolved, and the palladium tetrachloride is reduced to dichloride, which remains in solution; platinum is then precipitated, not by ammonium chloride, but by chloride of potassium. The precipitate so obtained is yellow, when pure, but red if iridium be present. After washing it with dilute solution of potassic chloride, it is ignited with twice its weight of potassic carbonate, thus obtaining metallic platinum, while at least a part of the iridium is left as teroxide insoluble in the aqua regia, which is afterwards used to dissolve the platinum freed from the fused mass by water.

The complete removal of iridium sometimes necessitates the repetition of these processes several times, after which the aqua regia solution of platinum is precipitated

by chloride of ammonium, and the spongy platinum, obtained on ignition, treated as already stated.

Even this product contains small quantities of osmium and silicon, to free it from which Deville and Debray recommend the fusion of the platinum by means of the oxyhydrogen blowpipe, in a cavity formed in a mass of lime. The silicon then combines with the lime as a slag and the osmium is volatilised as tetroxide.

The apparatus employed for this purpose is represented by fig. 384. The iron frame (*b*) is lined with well-burned lime in such a manner that a cavity is left for the metal and an opening (*d*) for running out the melted charge. To the upper part of the apparatus are attached two copper tubes (*e e*) fitted with platinum nozzles,

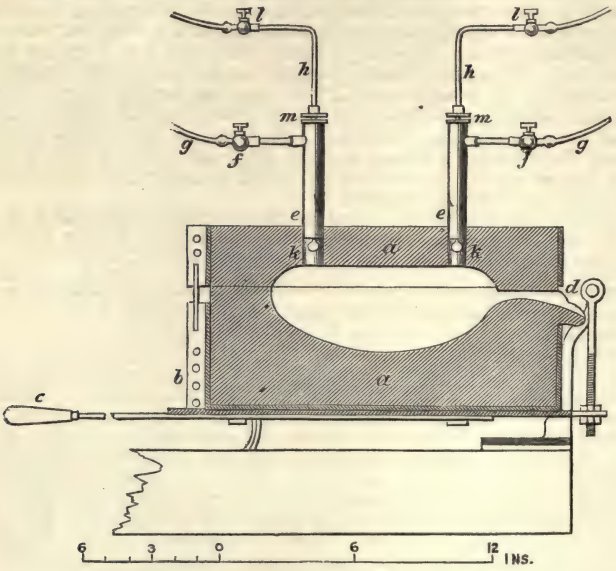


FIG. 384.

through which a mixture of oxygen gas and hydrogen or carburetted hydrogen is supplied for combustion by opening the cocks (*f f* and *l l*) in the supply tubes (*g g* and *h h*). The oxygen gas is supplied through the tubes (*h h*) and by means of the stuffing boxes (*m m*) they can be moved up or down as required. The handle (*c*) serves for tilting over the apparatus when the melted contents are run out through the opening (*d*) into moulds.

These same chemists also purify platinum by fusing the ore with galena in a reverberatory furnace. The lead forms an alloy with the platinum, from which the lead may be removed by cupellation.

Uses.—Platinum finds extensive use in chemical laboratories, where material is often required capable of withstanding a high temperature and the influence of strong re-agents.

The metal is also strongly employed for constructing stills used in the concentration of oil of vitriol. Sometimes these alembics are strongly gilt on the inside; for, unless protected in this way, the platinum made by Wollaston's process slowly becomes porous and admits of the transudation of the acid.

There are thirty-nine platinum alembics in use at twenty-six sulphuric works in France, and in Germany they are also much used; but they are not used to the same extent in England.

Scheurer-Kestner has proved that platinum is slowly dissolved by hot concentrated sulphuric acid; and, if traces of nitrous compounds are present, this action becomes more serious.

Platinum containing a little iridium is not nearly so subject to the action of sulphuric acid as the pure metal, but such impure metal is far harder to work.

Some years ago an attempt was made to introduce a platinum coinage into Russia, but the experiment was abandoned after a few years.

Compounds.—Platinum forms two series of compounds; the platinous or bivalent compounds and the platinic or quadrivalent combinations.

There are two oxides, PtO and PtO_2; two chlorides, $PtCl_2$ and $PtCl_4$, and double combinations of these with the chlorides of the alkali metals, as for instance $2KCl.PtCl_2$; $2KCl.PtCl_4$; $2NaCl.PtCl_6H_2O$; and $2NH_4Cl.PtCl_4$.

The bromides and iodides are analogous to the chlorides in composition.

There are also two sulphides, PtS and PtS_2, which correspond to the two oxides.

Sulphate and nitrate of platinum are also known, as well as sulphite $PtSO_3$.

Fulminating platinum ($Pt^{iv}H_2N_2$, $4H_2O$?), as it is called, is an insoluble black powder obtained by dissolving ammonic platinic chloride in caustic soda, and adding excess of acetic acid, or by precipitating the sulphate with ammonia. At 200° C. this compound suddenly explodes.

Besides the foregoing compounds, a large number of ammoniacal platinum compounds are known, which cannot be more than mentioned here.

Thus taking R to indicate a univalent radical, series of combinations are known representable by the formulæ—

$2NH_3.Pt''R_2$ $\quad$ $4NH_3.Pt^{iv}R_4$

$4NH_3.Pt''R_2$ $\quad$ $8NH_3.Pt_2{}^{iv}R_6O''$

$2NH_3.Pt^{iv}R_4$

Platinum may easily be alloyed with many other metals, the combinations being usually accompanied by evolution of light and heat.

The alloy, with 10 or 12 parts of silver to one of platinum, is completely soluble in nitric acid.

Copper and platinum in certain proportions form a brilliant alloy, while the alloy with iron is malleable and lustrous.

None of these alloys are used in the arts.

PLATINOUS OXIDE.

Formula PtO. Molecular Weight 213·1.

This substance is obtained on digesting platinous chloride in a solution of potash, and precipitation of the dark green solution by neutralisation with sulphuric acid; it is thus thrown down as a black hydrated powder.

This oxide is also formed when the dioxide is heated with a solution of oxalic acid; this gives a dark blue solution, which deposits fine copper-red needles of platinous oxide. The protoxide is soluble in acids and alkalies.

Platinous sulphite forms several double salts with the sulphites of the alkali metals, and among them the following is one of the most important—$3K_2SO_3.PtSO_33H_2O$.

PLATINIC OXIDE.

Formula PtO_2. Molecular Weight 229·1.

This oxide has a curious tendency to combine with alkaline bases. It may be prepared in several ways; best, perhaps, by precipitating a solution of platinic nitrate with half the quantity of sodic carbonate necessary for complete precipitation. Thus obtained, platinic oxide is a voluminous brown hydrate (PtO_2, $2H_2O$); on heating, the water is expelled, and on ignition, it parts with its oxygen, also leaving metallic platinum.

The solutions obtained by dissolving the dioxide in caustic alkalies give on crystallisation definite compounds; among them there is $Na_2O,3PtO_2,6H_2O$.

By dissolving this oxide in acids the various platinic salts may be obtained; they are of a reddish-yellow brown colour.

PLATINOUS CHLORIDE.

Formula $PtCl_2$. Molecular Weight 268·1.

Is obtained by gentle ignition of the tetrachloride at 235° C., when chlorine is expelled; the residue is of an olive colour and is insoluble in water, but dissolves in warm hydrochloric acid, and readily in caustic potash.

It may also be prepared by passing a current of sulphurous anhydride into a solution of platinic chloride, until the latter no longer gives a precipitate with ammonic chloride. When its hydrochloric acid solution is mixed with potassic chloride, there is deposited a red crystalline crop of $2KCl, PtCl_2$.

Such compounds as the latter, of which there are a great number known, are termed chloro-platinites or platinoso-chlorides.

PLATINIC CHLORIDE.

Formula $PtCl_4$. Molecular Weight 339·1.

This chloride is obtained as described upon the preparation of the metal; it is a deliquescent salt which crystallises in prisms. It is readily soluble in water, alcohol, and ether, and its solutions have a characteristic orange colour.

On evaporating its hydrochloric acid solution over lime and sulphuric acid, there are obtained crystals of the compound $2HCl, PtCl_4, 6H_2O$.

Platinic chloride unites with a great number of metallic chlorides, forming platino-chlorides or chloro-platinates. Thus beyond the ammoniacal double salt and the potassium salt, there are known also compounds with the chlorides of magnesium, manganese, zinc, iron, nickel, cobalt, cadmium, copper, etc.

Platinic chloride forms definite compounds with many alkaloidal bases, and with them and hydrochloric acid double salts of the hydrochlorides of the bases are obtained.

When the respective chlorides of platinum are submitted to the action of hydric sulphide, or the sulphydrate of an alkali metal, the corresponding sulphides are produced.

On ignition in a close vessel platinic sulphide PtS_2 loses half its sulphur, and becomes platinous sulphide PtS.

PALLADIUM.

Symbol Pd. Atomic Weight 106·5.

Palladium was discovered in 1803 by Wollaston, and obtained from platinum ore. It constitutes about 1 per cent. of the Columbian ore and from ¼ to 1 per cent. the Uralian ore of platinum, occurring in loose grains of a steel-grey colour and of sp. gr. 11·8 to 12·14.

It also occurs in Brazil as an alloy with gold, in many varieties of which it is found.

To extract the metal from the ore of platinum, this is dissolved in nitrohydrochloric acid, and the platinum removed by means of chloride of ammonium as described under that metal. The mother liquor is then precipitated by cyanide of mercury, when the palladium cyanide is precipitated as a pale yellow cyanide, which yields the metal on ignition; or the cyanide may be roasted with sulphur; this gives sulphide of palladium, which loses its sulphur on continued roasting, and furnishes the metal.

The metal may be also obtained from the gold alloy above referred to by the following process. The alloy is melted with 2 or 3 parts of silver, granulated and digested in nitric acid of 1·3 sp. gr.; the gold does not dissolve, while the palladium silver goes into solution, and this on treatment with salt gives a precipitate of argentic chloride.

The filtrate is concentrated after neutralisation by ammonia and yields a rose-coloured salt of ammonio-chloride of palladium in long silky crystals. These yield 40 per cent. of metal on ignition.

Instead of the foregoing proceeding, after precipitation of the silver as chloride, the following modification may be used.

Bars of zinc are introduced into the solution containing palladium, copper, lead and iron, when these metals are precipitated as a black powder upon the zinc. The precipitate is next dissolved in nitric acid, and supersaturated with ammonia, by which means the copper and palladium oxides are kept in solution, while the others

are precipitated. The clear mother liquor is now supersaturated with hydrochloric acid which throws down the sparingly soluble yellow double chloride, $PdH_6N_2Cl_2$. This on ignition gives metallic palladium.

Palladium is a very hard metal, white, ductile, and tenacious; more fusible than platinum, and more oxidisable than silver, tarnishing in the air at ordinary temperatures. According to Deville and Debray, it absorbs oxygen like silver does when melted, and spits on cooling. If heated on lime before the oxyhydrogen flame, it is dissipated in green vapours.

The metal is soluble in nitric or nitro-hydrochloric acids, but is not attacked to any great degree by other acids.

Palladium exhibits a curious power of absorption of hydrogen, which it gives out again in a high temperature.

It forms a carbide by holding the foil in a smoky flame.

It forms apparently three oxides; a suboxide Pd_2O corresponding to cuprous oxide, and like it forming a series of salts. It may be prepared by ignition of the hydrated protoxide.

The protoxide or palladous oxide PdO is a black powder obtained by igniting the nitrate; as a hydrate it is furnished by precipitating the solution of a palladous salt by an alkaline carbonate. This hydrated oxide is brown in colour and loses its water on heating.

The dioxide PdO_2 is obtained by adding caustic potash to the double palladic-potassic chloride ($2KCl, PdCl_4$); it forms a yellowish-brown hydrate.

Palladous chloride is obtained on evaporating to dryness a solution of the metal in aqua regia. It forms brown hydrated crystals which lose their water on heating and become black; on stronger ignition the metal is obtained. It forms double salts with the soluble chlorides and a series of ammonium compounds like those of platinum. Thus palladamine PdH_6N_2O is obtained from the salts $PdH_6N_2Cl_2$, and is a powerfully alkaline base forming definite salts.

Palladic chloride ($PdCl_4$) cannot be obtained in crystals, but it forms double salts which are crystalline. The compound $2KCl, PdCl_4$ consists of ruby red prisms.

The iodide PdI_2 may be obtained as a black powder by double decomposition; it is insoluble in water, but dissolves in ammonia.

A cyanide $PdCy_2$, a fluoride PdF_2, and a bromide are also known.

There appear to exist also three sulphides—palladous sulphide PdS; palladic disulphide PdS_2 (crystalline), and a subsulphide Pd_2S.

The protosulphide is prepared by heating the metal with sulphur, or by precipitating a salt of palladium with sulphuretted hydrogen.

The disulphide is obtained on fusing the monosulphide with potassic carbonate and sulphur.

Palladous sulphate $PdSO_4$ is obtained by dissolving the oxide in sulphuric acid or decomposition of the nitrate thereby.

The nitrate is yielded by dissolving the metal in nitric acid, and may be obtained in rhombic prisms.

All the ordinary salts of palladium when in the state of solution are red or brown.

The alloys of palladium.—Palladium forms alloys with antimony, arsenic, barium, copper, bismuth, gold, iron, lead, nickel, tin and platinum, etc.

The alloy with gold has a remarkably whitened appearance when the palladium amounts to 20 per cent. The native alloy from Porpez contains gold 85·98 per cent.; palladium 9·85 per cent.; silver 4·17 per cent. (Berzelius).

With eight times its weight of tin at a red heat palladium forms an alloy (Pd_3Sn_2) which is obtained in brilliant laminæ on digesting the mass in cold hydrochloric acid.

An alloy of palladium and silver is sometimes employed for making surgical instruments, as it does not tarnish in the air.

Sometimes also the metal is used in the construction of astronomical instruments and accurate balances, on account of the whiteness, hardness, and unalterability of palladium in the air.

Faraday and Stodart recommended an alloy of 1 part palladium with 100 parts of steel as one well adapted for cutting instruments.

The Wollaston medal of the Geological Society was formerly made of palladium.

RHODIUM.

SYMBOL Rh. ATOMIC WEIGHT 104·3.

This metal was discovered by Wollaston in 1803 in the ore of platinum. The platinum ore of Antioquia in Columbia contains about 3 per cent. Rhodium also occurs in the Ural ore and in the gold alloy of Mexico.

Under the head of palladium has been described the method by which that metal is extracted from platinum ores as cyanide; in the mother liquor there is contained rhodium, which may be isolated as follows. Hydrochloric acid is added and the whole evaporated to dryness. In this way the cyanogen is expelled and the metallic salts converted into chlorides. The dry mass is powdered and extracted with alcohol of 0·837 sp. gr., in which operation the double chlorides of sodium with platinum, iridium, copper and mercury are dissolved, while that with rhodium is left behind as a fine dark red powder. This on ignition gives the metal, or the latter may be obtained from the double chloride by treating it gently in a glass tube in a stream of hydrogen; on then washing out the residual sodic chloride the metal is left behind.

More recently Deville and Debray have described another process for the extraction of rhodium.

The platinum residues are fused with an equal weight of lead and twice their weight of litharge. In this way a button of lead is obtained containing all the metals less oxidisable than lead, and this is heated with nitric acid (1 : 1), which removes, besides the lead, the copper and palladium. The insoluble powder is mixed with five times its weight of peroxide of barium, and heated to redness for several hours in a clay crucible. The mass is then heated with water, and afterwards with aqua regia to remove the arsenic acid. Sulphuric acid is next added to exactly precipitate the barium, the liquid boiled, filtered, and evaporated first with a little nitric acid and afterwards with much ammonic chloride. The mass, dry at 100°C., is extracted with a concentrated solution of chloride of ammonium, which dissolves the rhodium, and from the solution the chloride of ammonium is expelled by evaporation. Finally nitric acid is added and the evaporation is completed in a porcelain crucible. The mass is now moistened with sulphide of ammonia mixed with sulphur, and ignited for some time, when metallic rhodium is obtained.

Rhodium is less fusible than platinum, but oxidises like palladium. In appearance it resembles aluminum, and when pure is ductile and malleable after fusion. Its density is then 12·1. Rhodium is oxidised by fusion with a mixture of nitre and potassic carbonate. It is also oxidised by acid potassium sulphate, giving a double sulphate $KRo2SO_4$, while sulphurous anhydride escapes.

Heated in contact with salt in a stream of chlorine, a double chloride results, $3NaCl, RoCl_3$.

Berzelius and others have contended for the existence of three chlorides, but according to Claus, there is but one definite chloride, viz. the one with the composition $RoCl_3$. It may be obtained anhydrous, by igniting the powdered metal in chlorine, and as thus prepared it is insoluble. By decomposing potassic rhodic chloride by silicofluoric acid, potassic fluosilicate is formed, and may be filtered off, while a solution results which, on evaporation, gives the chloride of rhodium as a red-brown mass of composition $RoCl_3, 4H_2O$. If to a solution of rhodic chloride excess of ammonia be added, and the mixture boiled, a yellow compound is precipitated which may be purified by re-crystallisation; it has the formula $RoCl_3, 5NH_3$. When ignited the compound yields pure rhodium.

Rhodic oxide Ro_2O_3 is the only oxide which gives rise to salts. It is produced by the oxidation of the metal by a fused mixture of nitre and potassic carbonate.

A hydrate $Ro_2O_3 5H_2O$ is also known and three other oxides—viz. a green-coloured hydrate of the oxide RoO_2; a trioxide RoO_3 which is blue, and a protoxide RoO.

Rhodium when heated in the vapour of sulphur gives protosulphide RoS.

The sesquisulphide Ro_2S_3 is prepared as a brown hydrate by decomposing a hot solution of sodio-rhodic chloride with potassic or sodic sulphide.

The acetate is an amorphous orange-yellow body, whilst the nitrate and sulphate are both crystalline. Several phosphates and a cyanide are known. The salts of rhodic oxide are chiefly of a rose-red colour and are decomposed by iron or zinc with the production of metallic rhodium.

The alloys of rhodium, so far as they have been studied, appear to be true chemical compounds, as evidenced by the heat evolved in combination. The zinc alloy resists the action of hydrochloric acid. The alloy with tin is crystalline, black, and fusible only at a very high temperature.

A native alloy of gold and rhodium found in Mexico contains from 34 to 43 per cent. rhodium.

An alloy made from 1 part of rhodium and 1 part of steel has a specific gravity of 9·176, and is of fine colour, and does not tarnish in the air.

RUTHENIUM.

SYMBOL Ru. ATOMIC WEIGHT 104·2.

This metal was first shown to exist by Claus, who discovered it in an ore of platinum. Since then the metal and its compounds have been carefully examined by Fremy and Deville and Debray.

It is found chiefly in osmiridium, which contains from 3 to 6 per cent., but it is not found in that part of the platinum ore soluble in aqua regia.

From this last-mentioned source the metal may be extracted after the method of Fremy. After exhausting the ore with aqua regia, the residue containing osmium, iridium, ruthenium, and rhodium, together sometimes with titaniferous and chrome iron, is roasted in a current of dry air in a porcelain or platinum tube. The tube is connected with some glass flasks, and where the tube projects from the furnace it is plugged with some fragments of porcelain.

During the oxidation the osmium is converted into tetroxide, which, owing to its superior volatility, is carried over and condensed in needles in the glass flasks, while the ruthenium becomes dioxide, and this being less volatile deposits in regular square prisms upon the broken porcelain. By heating this oxide in a current of hydrogen, the metal is obtained as a dark grey powder.

Ruthenium is a very hard, brittle metal, which is difficultly fusible even in the oxyhydrogen blowpipe. Deville and Debray have assigned a sp. gr. of 11·0 to 11·4 to the melted metal. By fusion with nitre and caustic potash, the metal gives an orange-coloured soluble ruthenate, and on saturating a solution of this salt with chlorine, there is obtained hyper-ruthenic acid RuO_4, the analogue of osmic acid OsO_4; hyper-ruthenic acid is volatile, and condenses in golden crystals or globules.

Deville and Debray in their later researches have employed this body as the source of their purest metal. A solution of hyper-ruthenic acid in potash gives with alcohol oxide of ruthenium RuO_2, and this, on reduction with coal gas at an elevated temperature, yields the pure metal. When obtained from one of its ammoniacal chlorides by calcination it is a white spongy mass.

Ruthenium forms five oxides with the formulæ, RuO, Ru_2O_3, RuO_2, RuO_3, RuO_4. The higher oxide has already been described; it is incapable of combination with bases. When dropped into potash it is dissolved slowly, oxygen is evolved, and a green salt crystallises out which has the formula KRu_2O_5.

The oxide RuO_3 (ruthenic anhydride or ruthenic acid) is insoluble in water; it may be obtained on fusing any of the other oxides with nitre. The sesquioxide is the most stable basic oxide of ruthenium, and is prepared by igniting the metal in a current of air; it is of a deep blue colour and insoluble in acids. As a hydrated oxide Ru_2O_3, $3H_2O$, it is precipitated from the trichloride as a bulky blackish-brown powder which forms salts with acids.

The dioxide RuO_2 is formed by roasting the disulphide, or by strongly igniting the sulphate $Ru2SO_4$.

The protoxide is prepared by calcining the dichloride with carbonate of sodium in a current of carbonic anhydride and dissolving out the soluble part of the product by water. This oxide is of a dark grey colour and metallic lustre, and is not acted upon by acids.

Three chlorides of ruthenium are known—viz. $RuCl_2$, $RuCl_3$, and $RuCl_4$.

The most important is the trichloride, which may be obtained by dissolving the hydrated sesquioxide in hydrochloric acid; on evaporation there results a yellowish crystalline mass of the salt which is soluble in alcohol. Not only does this chloride form double salts with the chlorides of potassium and sodium, but also a number of ammoniacal basic salts corresponding to those obtainable from platinic chloride.

Two sulphides of ruthenium are known, sesquisulphide Ru_2S_3, and a disulphide RuS_2. The first of these is obtained by conducting sulphuretted hydrogen into the

blue solution of the protochloride. When the same gas is passed for a long time into a solution of the trichloride, the disulphide is formed as a brown yellow precipitate.

Two alloys of ruthenium are well known; one with zinc which crystallises in regular hexagonal prisms which take fire when heated in the air and burn with deflagration.

The alloy of tin and ruthenium $RuSn_2$ is obtained by heating ruthenium to redness with about ten times its weight of tin, in a graphite crucible, and dissolving out the excess of tin from the product with hydrochloric acid. The alloy is thus obtained in fine cubic crystals, resembling those of melted bismuth.

IRIDIUM.

Symbol Ir. Atomic Weight 198.

History and Occurrence.—Iridium was discovered simultaneously with osmium by Smithson Tennant in 1804 in the black scales which remain undissolved when platinum ore is extracted with nitro-hydrochloric acid. The same alloy, which is known as iridosmine, occurs also in flat metallic grains in native platinum.

Characters.—Iridium is a hard, white, brittle metal, which requires the heat of the oxyhydrogen blowpipe or that of a strong voltaic current to melt it. After fusion it has a density of 21·15. When heated in a finely divided state in the air, it absorbs oxygen, but is not oxidised when in the massive state. Alone it is not acted upon by acids or even by nitro-hydrochloric acid, but when alloyed with platinum aqua regia readily dissolves it.

By fusion with nitre or caustic alkalies the metal is oxidised. By decomposing a solution of the sulphate with alcohol, iridium may be obtained as a black powder, possessing characters corresponding to those of platinum black.

Preparation.—Iridium may be prepared most easily by reducing the native alloy to powder, mixing it with common salt, and heating the mixture to redness in a glass tube, through which a stream of moist chlorine gas is transmitted; to the extreme end of the tube a receiver containing ammonia is attached. In this way the respective chlorides of osmium and iridium are formed, and the former of these being volatile is carried over by the chlorine into the alkaline solution by which it is decomposed, forming osmic acid and hydrochloric acid, which then combine with the ammonia. The chloride of iridium remains behind in the tube, and is dissolved out together with sodic chloride by water; the solution thus obtained is evaporated with sodium carbonate to dryness, and the mixture then ignited. After this the mass is extracted with water, dried, and the residue of ferric oxide and oxide of iridium, in combination with soda, is reduced by hydrogen at a high temperature. By extracting the residue with water and strong hydrochloric acid the iron and alkali are removed, and there remains metallic iridium. Or the metal may be prepared by precipitating ammonic iridic chloride from the solution of mixed chlorides above described, and igniting the precipitate. But the metal so obtained is liable to be contaminated with ruthenium.

Compounds.—Iridium forms three series of compounds related to the three oxides as follows. Monoxide or hypoiridious oxide, IrO; iridious or sesquioxide, Ir_2O_3; and iridic oxide, IrO_2. There is a fourth or periridic oxide, IrO_3, which is not known in the free state.

The monoxide (IrO) is formed when an alkaline hypochloriridite is decomposed by caustic alkali in an atmosphere of carbonic anhydride. It quickly oxidises in the air.

The sesquioxide (Ir_2O_3) is formed when the metal is oxidised by fusion with nitre or caustic alkali, or when it is heated in a pulverulent state in the air.

According to Claus, a hydrate of the dioxide (IrO_2, $2H_2O$) is formed on boiling a solution of iridic trichloride with caustic potash, when the substance is precipitated as an indigo-coloured powder. On ignition it becomes anhydrous.

There are three chlorides of iridium of the formulæ $IrCl_2$, $IrCl_3$, and $IrCl_4$; all these form double salts with the chlorides of the alkali metals.

On heating the double salt of trichloride of iridium ($3KCl$, $IrCl_3$. $3H_2O$) with hydric potassic sulphite in solution, until the green colour passes into red, and

evaporating the solution, the dichloride of iridium is obtained as a double salt in red crystals $4KCl.\ IrCl_2,\ 2K_2SO_3,\ IrSO_3,\ 12H_2O$.

The trichloride is the most stable of the three chlorides, and is obtained as a black sublimate on heating the metal in a current of chlorine. It is known to form a compound of the composition $2IrCl_3.\ 3Hg_2Cl_2$.

The tetrachloride ($IrCl_4$) is prepared by dissolving the metal or any of its oxides in aqua regia.

An iridic tribromide ($IrBr_3,\ 4H_2O$) may be obtained in olive brown crystals, and three iodides are known, viz., IrI_2, IrI_3, and IrI_4.

Corresponding to the three principal oxides there are three sulphides which may be obtained by decomposing the respective chlorides with sulphuretted hydrogen.

The alloys of iridium are very interesting, and a number of them have been studied, such as those with gold, copper, lead, mercury, osmium, platinum, silver, tin, and zinc.

The native alloy of osmium and iridium is used, by reason of its hardness, to point metallic pens.

OSMIUM.

Symbol Os. Atomic Weight 199·2.

History and Occurrence.—Osmium, as stated elsewhere, was discovered in the ore of platinum in 1803 by Tennant. Its most plentiful source is the native osmiridium.

Preparation.—The metal may be extracted from osmiridium or platinum residues, resulting after extraction of the ore by aqua regia, by several methods which have undergone simplification at the hands of Fremy. Perhaps the simplest process consists in preparing the tetroxide of osmium as described under 'Iridium,' and treating this with hydrochloric acid and mercury at 140° C., in a closed vessel, when the following reaction results:—

$$OsO_4 + 8Hg + 8HCl = Os + 4Hg_2Cl_2 + 4H_2O.$$

On evaporation the water and excess of acid are expelled, and by distilling the residue in a retort the mercury and calomel pass over, leaving pure metallic osmium in a pulverulent form behind.

The metal may also be obtained by igniting ammonium chloro-osmite with sal-ammoniac.

Characters.—The properties of osmium differ somewhat according to the mode of preparation. When in the pulverulent state it is black and only acquires a metallic lustre by burnishing. When exposed to a damp atmosphere it emits an odour of the tetroxide, and, when set on fire in the air, it burns away entirely into the same volatile body. Osmium which has been once heated to the melting point of rhodium will not burn in the air, until heated above the melting point of zinc. Deville and Debray obtained the metal in a compact state by reduction of the sulphide with gas coke in a closed retort at about the melting point of nickel. Obtained thus it is brittle, and has a blue cast of colour like that of metallic zinc.

In the pulverulent state the metal has a density of 10, but after heating to the melting point of palladium its density becomes 21·4. Osmium is the least fusible of all metals, and possesses characters approaching those possessed by arsenic and antimony.

Combinations.—Five oxides of osmium are known of the formulæ here given: OsO, Os_2O_3, OsO_2, OsO_3, and OsO_4.

The protoxide is obtained by heating hypo-osmious sulphite in carbonic anhydride; it is a dark greenish powder almost insoluble in acids; its hydrate is bluish-black and dissolves in hydrochloric acid forming an indigo-coloured solution of the dichloride $OsCl_2$.

The sesquioxide (Os_2O_3) is unknown in the free state, although it is said to be obtained by heating either of the double salts of the trichloride with sodium carbonate in a stream of carbonic anhydride.

The dioxide is a black powder obtained by heating a mixture of potassic osmio-

chloride with sodic carbonate in carbonic anhydride. As a hydrate (OsO_2, $2H_2O$) it is formed on precipitating potassic osmiochloride with potash.

The trioxide is only known in combination with alkalies as osmites; the potassium salt is $K_2O.OsO_3.2H_2O$ and is a rose-coloured crystalline powder. This salt is readily obtained on heating a solution of the tetroxide in potash with a little alcohol. On digesting the salt so obtained in ammonic chloride, a yellow salt is obtained of the composition ($2NH_4Cl$, OsO_2, N_2H_4), and this on ignition in hydrogen gives pure osmium.

The tetroxide forms colourless acicular transparent crystals which melt below 100° and boil at a temperature somewhat higher. The vapour of this oxide is irritating and excessively poisonous. It is a powerful oxidising agent, and gives a characteristic blue precipitate when its solutions are mixed with tincture of galls. It does not form salts.

Three chlorides of osmium are known, corresponding to those of iridium and ruthenium. Osmious chloride ($OsCl_2$) is the product of the action of chlorine gas upon the metal; it dissolves in water to a violet colour, and gives double salts of a green colour.

The tetrachloride ($OsCl_4$) is produced in the same way as the dichloride, using excess of chlorine; it is a volatile, red, crystalline, fusible powder which is soluble in water, and is then decomposed into tetroxide and hydrochloric acid, a decomposition which is also accompanied by the deposition of some dioxide.

A double salt of the formula $2KCl.\ OsCl_4$ is known, and also one represented by ($2AgCl.\ OsCl_4$).

The trichloride ($OsCl_3$) and the hexachloride ($OsCl_6$) are only known in combination as double salts.

Osmium gives with ammonium salts a number of interesting combinations; thus when the tetroxide is heated with much ammonia, there is obtained $N_2H_6OsO_2\ H_2O$, and if potash be present we get $K_2N_2Os_2O_5$, or potassic osmiamate as it is called. This is a yellow crystalline body of a detonating character.

A tetrasulphide of osmium appears to be the best known sulphide; there are said to be others corresponding to the various oxides, and obtained by decomposition of the chlorides with sulphuretted hydrogen.

Osmium also combines with phosphorus, etc.

The native alloy, osmium-iridium or irodosmine, gave by analysis the following percentages (Berzelius): iridium 46·77; osmium 49·35; iron 0·74; rhodium 3·15.

IRON.

Symbol Fe. Atomic Weight 56.

History.—This metal was known at a very remote period, and many of the references to it in ancient writings are of a mythical character. The Greek and Roman names— χάλυψ and *chalybs*—are considered to have been derived from the name of a tribe of people that lived on the shores of the Black Sea, and were especially skilled in the art of working iron, or that form of the metal which is now called steel.

Occurrence.—Iron occurs naturally to some extent in the metallic state, constituting the chief mass of some meteorites, while in others it is disseminated throughout an earthy matrix. Metallic iron also occurs associated with platinum in some ferruginous deposits, and disseminated through the mass of basaltic rocks. Meteoric iron always contains nickel, sometimes also cobalt, copper, chromium, and tin, as shown by the following tabular statement of analyses:

	Berzelius		Trehole		Jackson	Morren	Sillman and Hunt	Stromeyer
Iron	93·78	88·04	89·78	85·61	66·56	83·57	92·58	81·8
Nickel	3·81	10·73	8·89	12·27	24·71	12·67	5·71	11·9
Cobalt	·21	·46	·67	·89	—	—	—	1·0
Copper	—	·07	—	—	—	—	—	—
Manganese	—	·13	—	—	3·24	—	—	·2
Chromium	—	—	—	—	—	—	—	—
Tin	—	trace	—	—	—	—	—	—
Magnesium	—	·05	—	—	—	—	—	—
Arsenic	—	—	—	—	—	—	trace	—
Sulphur	—	trace	—	—	4·0	—	—	5·1
Ferrous sulphide	—	—	—	—	—	2·30	—	—
Carbon	—	·04	—	—	—	—	—	—
Chlorine	—	—	—	—	1·48	·91	—	—
Insoluble	2·20	·48	—	—	—	—	1·40	—
	100·0	100·0	99·34	98·77	99·99	99·45	99·69	100·0

Iron occurs, however, far more frequently and in much greater abundance in various states of combination with oxygen as magnetite, hematite, or specular iron.

Compounds of ferrous oxide or ferric oxide with various acid oxides also occur abundantly: the carbonate as spathic iron; the phosphates as vivianite, dufrenite, and in several other minerals; the arsenates as shorodite and cube ore, etc.; the silicates as fayalite, and in a great number of other minerals; the titanate as iserine, ilmenite, and the various kinds of titaniferous iron ore; the chromate as chrome-iron ore; the tantalate as columbite; the tungstate as wolfram. Iron also occurs in various states of combination with sulphur as pyrites, and with arsenic as arsenosiderite. Iron in various states of combination is likewise very widely distributed, and there are few natural bodies in which this metal is not present to some extent. It exists in the ashes of most plants, and appears to be an essential constituent of the blood of animals.

Characters.—Iron is a moderately soft metal, resembling silver in whiteness; it is capable of acquiring a very high lustre when polished, and is extremely tenacious. The specific gravity varies from 7·6 to 8·14, according to the mode in which the metal has been worked. The crystalline form of iron is either the cube, octahedron, or some other form belonging to the regular system.

Though iron is the most abundant of the heavy metals, and is most largely employed in the arts, it is very rarely met with in a state of absolute chemical purity. Owing to the fact that it readily combines with or retains in a state of admixture various other elementary substances, such as carbon, oxygen, phosphorus, sulphur, silicon, etc., the metallic iron ordinarily used contains some one or more of those substances in varying amount, and the physical characters of the metal are very materially influenced by the nature as well as the proportion of the admixtures it contains. It is to this circumstance that the differences between the three forms of iron known as malleable iron, pig iron, and steel, are referrible; and it appears to be chiefly the amount of carbon in iron which determines those remarkable differences in virtue of which iron has such a wide range of applicability to a great variety of purposes.

The distinction between the three kinds of iron is not by any means absolute, but is marked rather by the extent to which particular characters are developed in association with others. Iron containing a large proportion of carbon melts at a temperature comparatively much lower than that required for melting the pure metal; but at the same time its malleability is so much inferior to that of iron containing only a very small proportion of carbon, that it cannot be wrought under the hammer. Iron which contains but little carbon, and is malleable, has also a much higher degree of toughness or tenacity than pig iron, which on the other hand is very much harder. On account of these differences iron which approaches nearest to a state of purity is termed malleable iron, while that which is highly carburetted and capable of being wrought by smelting is termed cast iron. Intermediate between these two kinds of iron is steel, which combines some of the peculiarities of malleable iron and cast iron, since it can be melted as well as forged and rendered hard or soft at will; or, as it is technically termed, tempered, by cooling it suddenly or gradually.

Leaving out of consideration for the present all other substances met with in iron except carbon, it appears that the greater or less approximation to the character of pure iron is so uniformly accompanied by very slight differences in the amount of carbon in the metal, that these two circumstances must be regarded as having a very intimate causal connection.

Compounds.—Iron forms two classes of compounds—namely, the ferrous combinations in which it behaves as a dyad, as in ferrous oxide, or the corresponding sulphate and chloride; and the ferric compounds in which iron is trivalent—for example, ferric chloride (Fe_2Cl_6).

The vapour density of this last named substance, as determined by Deville, would seem to indicate that in ferric chloride the metal is tetratomic; the compound would therefore have a rational formula as follows:

$$Cl_3Fe—FeCl_3.$$

The three oxides have the formulæ FeO Fe_2O_3 and Fe_3O_4, and the sulphides are represented by Fe_2S, FeS, FeS_2 F_2S_3. Iron forms apparently two other sulphides with the formulæ Fe_7S_8 and Fe_3S_4. The former of these, both of which are termed magnetic sulphides, is often formed together with ferrous sulphide when sulphur and iron are heated together; it is soluble in hydrochloric acid.

There are two chlorides ($FeCl_2$ and Fe_2Cl_6) and corresponding bromides, iodides, and fluorides; two sulphates, nitrates, and phosphates. Ferrous carbonate ($FeCO_3$) is a well-defined body, and beyond these there are a number of compounds of less importance.

Ferrous oxalate, $2FeC_2O_4$. $3H_2O$, is occasionally met with in the native state, as humboldite or iron-resin, which is formed in the brown-coal strata. It may be prepared by double decomposition or by exposing ferric oxalate in presence of free oxalic acid to sunlight; carbonic anhydride is then evolved, and ferrous oxalate is precipitated in a crystalline form with two molecules of water.

Ferric oxalate, which is a yellow salt, nearly insoluble in water, may also be prepared by double decomposition.

Ferrous hydric phosphate, $Fe''HPO_3$, is precipitated as a white powder, when a solution of trisodic phosphate is added to one of a ferrous salt.

The native blue phosphate or vivianite has been already spoken of.

A ferric phosphate, $Fe_2''P_2O_8$ $4H_2O$, is obtained as a white powder by precipitating ferric chloride by an alkaline orthophosphate.

Several silicates of iron exist, notably ferrous orthosilicate 2FeO. SiO_2, which constitutes for the most part 'finery slag.'

Ferrous nitrate, $Fe2NO_3$, results from the action of cold dilute nitric acid upon the protosulphide of iron. When its aqueous solution is evaporated in a vacuum, it forms pale green crystals $Fe2NO_3,6H_2O$, which are liable to change.

Ferric nitrate, $Fe3NO_3$, is produced by the action of tolerably strong nitric

acid upon the metal; it is of a deep red colour, and its solution is used as a mordant in dyeing.

Several basic nitrates also exist.

Diferrous phosphide, Fe_2P, is produced when the phosphate is reduced with charcoal.

A silicide of the formula Fe_2Si also is known, and it is probable that the compound FeSi exists.

A nitride of the composition N_2Fe_4 was obtained by Stahlschmidt.

The alloys of iron are not of great importance, although such combinations with most of the metals are known. When iron contains more than traces of silver, copper, arsenic, or antimony, it is rendered what is termed red short, which quality is considered defective.

Galvanised iron is used largely for roofing, etc., and is prepared by immersing clean sheet iron in a bath of molten zinc; if the iron be first coated with a thin film of tin by means of voltaic deposition, it furnishes a superior kind of galvanised iron. The zinc protects the iron from oxidation.

Deville and Caron obtained an alloy of the formula Fe_2Sn, and another of the composition FeSn is also known.

Among many other alloys of iron, one of the formula Fe_4K has been also described.

FERROUS OXIDE.

Formula FeO. Molecular Weight 72.

This oxide constitutes the base of the ferrous salts, and is isomorphous with magnesia, etc.

It is obtained as a hydrate when a ferrous salt is precipitated by an alkali; in this form it is nearly white, but on boiling the mixture water is given off, and the precipitate turns black. Ferrous oxide, from its affinity for oxygen, is an unstable body; on exposure it turns reddish-brown from formation of ferric oxide Fe_2O_3. This tendency to oxidation is also exhibited by all ferrous solutions, which pass on exposure to the air into a higher state of oxidation—a change which is often accompanied by the formation of insoluble basic salts. Ferrous acetate seems to admit most readily of atmospheric oxidation. Ferric acetate is of a blood-red colour.

FERRIC OXIDE.

Formula Fe_2O_3. Molecular Weight 160.

History.—The compounds of iron with oxygen, though known and used at a very remote period, were not fully distinguished from each other as regards their chemical composition until the end of the eighteenth century. Iron rust was used by Æsculapius medicinally, and forge scale, *σκωρία σιδήρου*, was described by Dioscorides as a similar but less effective remedy. Bloodstone, or *αἱματίτης*, was also mentioned by this author, and it was regarded by Pliny as a variety of *sideritis*, or magnetic iron ore. In Geber's works red oxide of iron is termed *crocus martis*, while Basil Valentin gave it the name of colcothar, and in 1735 the black oxide was known by the name of *æthiops martis*. Scheele was the first to indicate, in 1777, the fact that in these substances iron was combined with oxygen in different proportions; this view was further developed in 1782 by Lavoisier, and finally brought to its present position by Berzelius.

Occurrence.—Ferric oxide occurs very abundantly in a variety of forms; it occurs beautifully crystallised as specular iron ore in Elba and other places. As red hematite or bloodstone it occurs in compact and amorphous masses, and constitutes an important iron ore. There are several native hydrates of this compound known as brown hematite, göthite, and bog iron ore.

Characters.—Ferric oxide is not so powerful a base as ferrous oxide; it may be prepared by precipitation of a ferric salt in solution by an alkali, as a reddish-brown bulky hydrate which loses its water on ignition. When in fine powder this oxide has a fine red colour which renders it available for use as a pigment, and it is prepared on a large scale for this purpose by calcination of ferrous sulphate.

The hydrated oxide is readily soluble in acids; the anhydrous oxide is not so readily dissolved, and the salts formed have a tendency to produce basic compounds.

A number of hydrates of this oxide are known.

Mixed with sawdust, hydrated ferric oxide is used in Hill's process for separation of sulphuretted hydrogen from coal gas. There is thus produced ferrous sulphide and free sulphur, as shown by the following equation:

$$Fe_2O_3 + 3H_2S = 2FeS + S + 3H_2O,$$

and when the product is exposed to the air (or 'rarefied') ferric oxide is reproduced, and more sulphur therefore set free; in this way the oxide may be constantly renewed.

Ferric oxide plays towards some bases the part of a feeble acid. Thus Pelouze has described a compound he obtained of the formula

$$4CaO,Fe_2O_3.$$

FERROSO-FERRIC or MAGNETIC OXIDE.

Formula Fe_3O_4. Molecular Weight 232.

This compound, known also as loadstone and black oxide, is supposed to acquire its magnetic character from the inductive influence of the earth. In its various native forms occurring in beds and constituting even mountains, sometimes found in Sweden, America, etc., it constitutes one of the most valuable ores of iron.

It may be formed artificially by mixing due proportions of ferrous and ferric salts, and adding to the mixed solution an excess of alkali; on boiling the two hydrates combine and form minute crystals of magnetic oxide.

If recently precipitated hydrated ferric oxide be boiled with water and iron turnings in excess added, then hydrogen is evolved and magnetic oxide is produced. It is also produced when metallic iron is exposed at an elevated temperature to the presence of steam; in this way at 500°F. or 1000°F. the iron becomes coated with magnetic oxide as a continuous compact layer on the surface not liable to change by atmospheric influences or even by dilute acids; and Professor Barff has recently proposed the application of this process to iron goods, such as rails, cooking utensils, lamp-posts, gas-pipes, etc., in order to avoid the rusting to which such articles are ordinarily subject when exposed to a damp atmosphere.

Magnetic oxide is soluble in acids; it does not form specific salts, but yields a mixture of ferrous and ferric salts, thus

$$Fe_3O_4 + 4H_2SO_4 = FeSO_4 + Fe_23SO_4 + 4H_2O.$$

FERRIC ACID.

Formula H_2FeO_4. Molecular Weight 122.

Although this compound has not been prepared in the free state, its barium, strontium, and calcium salts may be obtained by mixing solutions of the earths with potassium ferrate, which is obtained as follows:

A mixture of ferric oxide with four times its weight of nitre, is heated to redness during an hour in a covered crucible, and the resulting brown deliquescent mass is treated with ice-cold water which gives a violet-coloured solution from which the potassic ferrate may be precipitated by a strong alkali.

It may also be made by suspending recently precipitated hydrated ferric oxide in a strong solution of potash, and submitting the mixture to a current of chlorine gas; it is then deposited as an amorphous black powder which can be drained upon a tile.

Potassic ferrate is an unstable salt readily decomposed by organic matter, or by exposure to a temperature of 100°C; acids resolve it into free oxygen and ferric oxide.

FERROUS CHLORIDE.

Formula $FeCl_2$. Molecular Weight 127.

This salt may be obtained in the anhydrous state by passing hydrochloric acid gas over red-hot iron, hydrogen being evolved $Fe + 2HCl = FeCl_2 + H_2$; the white salt which forms sublimes at a temperature of melting glass.

Ferrous chloride may also be obtained by dissolving iron in hydrochloric acid; the concentrated solution yields crystals of the composition $FeCl_2, 4H_2O$, and of a green colour.

Ferrous chloride is also formed when ferric chloride is heated in a current of

hydrogen. It is a deliquescent salt, soluble in water and alcohol, and liable to undergo atmospheric oxidation. When heated in the open air, it loses chlorine and forms ferric oxide.

Ferrous chloride forms a double salt with ammonic chloride.

FERRIC CHLORIDE.

Formula Fe_2Cl_6. Molecular Weight 325.

This salt may be prepared by dissolving ferric oxide in hydrochloric acid; on evaporation of the solution to a low bulk, red hydrated crystals Fe_2Cl_6, $6H_2O$ are deposited, which are exceedingly soluble in water and alcohol. It may be prepared in the dry state by passing chlorine over iron heated to redness. The salt sublimes in lustrous scales; it also crystallises with $10H_2O$ and $12H_2O$. With ammonic chloride it furnishes a double salt which crystallises in cubes, and with other chlorides other double salts are obtained.

FERROUS IODIDE.

Formula FeI_2. Molecular Weight 310.

This preparation, which is used in medicine, is made by digesting one part of iron wire in water containing four parts by weight of iodine. The iodide thus produced gives to the solution a pale green colour, and on evaporation in vacuo crystals of the composition FeI_24H_2O are obtained. The salt may be rendered anhydrous by heating, and is then fusible. By atmospheric oxidation it is resolved into iodine and hydrated ferric oxyiodide.

FERROUS SULPHIDE.

Formula FeS. Molecular Weight 88.

Occurrence.—This substance does not occur naturally in a separate state, except in some meteorites; but it occurs combined with ferric sulphide, as pyrrhotin or magnetic pyrites, 5FeS, Fe_2S_3; with nickel sulphide, NiS2FeS; with antimonous sulphide in several proportions, as berthierite and haidingerite; with zinc sulphide in some kinds of blende and in some kinds of fahl-ore. Ferrous sulphide is a constituent of the different kinds of regulus obtained in smelting ores of lead and copper.

Characters.—Ferrous sulphide, prepared in the compact state, by melting together iron and sulphur, is a heavy substance of a yellowish colour and metallic lustre. As obtained by mixing a solution of a ferrous salt with alkaline sulphide, it is black, amorphous, pulverulent and is probably hydrated, sometimes presenting a distinct green tinge when very finely divided. Ferrous sulphide melts at a full red heat and is not decomposed when heated to whiteness out of contact with air; but, when heated moderately in contact with atmospheric air, it is gradually oxidised and converted into ferrous sulphate. In the compact state it is but little altered by exposure to the air at the ordinary temperature; but, as obtained by precipitation from the solution of ferrous salts by alkaline sulphides, it oxidises rapidly when exposed to the air, and is converted into ferrous sulphate which by further oxidation is converted into basic ferric sulphate.

Ferrous sulphide is readily decomposed by acids, generally with evolution of sulphuretted hydrogen and formation of a ferrous salt; nitric acid converts part of the sulphur into sulphuric acid with evolution of nitrous vapours, and part of the sulphur is precipitated. Heated to redness in contact with water vapour it is decomposed; hydrogen and sulphuretted hydrogen are given off, and the iron remains in the state of ferroso-ferric oxide, which retains a portion of the sulphur. Ferrous sulphide is not affected by chlorine at the ordinary temperature, but when heated in contact with the gas it is converted into sulphur chloride and ferric chloride. When melted with alkalies, alkaline carbonates, or alkaline earths, it is partly decomposed and some alkaline or earthy sulphide is formed; melted with a large proportion of lead oxide the whole of the sulphur is oxidised to sulphurous oxide, metallic lead is separated and ferrous oxide formed, which remains mixed with the undecomposed lead oxide.

The black mud deposited at the bottom of drains, cesspools, ponds, etc., where ferruginous substances are in contact with decomposing organic materials, contains

ferrous sulphide, and its formation is probably due in part to the deoxidation of sulphates by the putrefying substances. On exposure to the atmosphere this mud often evolves sulphuretted hydrogen.

Preparation.—Ferrous sulphide may be prepared by melting together sulphur and some excess of iron filings, or by holding a stick of sulphur against a red-hot bar of iron. When a mixture of iron filings and sulphur is moistened with water, and warmed, combination takes place suddenly with considerable evolution of heat. Ferrous sulphide is also produced when dry ferrous sulphate is ignited with charcoal out of contact with air, when ferrous sulphate is in contact with decomposing organic substances, when magnetic pyrites, ferric sulphide, or iron pyrites are heated to bright redness in contact with hydrogen, or with metallic iron out of contact with air, and by precipitation from ferrous salts by alkaline sulphides.

FERRIC SULPHIDE.

FORMULA Fe_2S_3. MOLECULAR WEIGHT 208.

This substance is probably a constituent of magnetic pyrites, copper pyrites and some other minerals, but it does not otherwise occur naturally. It may be prepared by heating iron or ferric oxide with excess of sulphur; when ferric oxide is used, the operation requires to be repeated several times in order to decompose the whole of the ferric oxide.

Ferric sulphide is also formed by the action of sulphuretted hydrogen upon ferric axide at 100°, or upon ferric hydrate at the ordinary temperature, and by dropping o solution of neutral ferric sulphate into excess of ammonium sulphydrate. When dried out of contact with air, it is a yellowish-grey substance; it is not magnetic when moist, and oxidises very rapidly on exposure; acids decompose it with formation of the corresponding ferrous salt, disengaging sulphuretted hydrogen and precipitating sulphur. When heated to redness in a close vessel sulphur is given off, and the residue consists of magnetic pyrites. Heated in contact with atmospheric air it is oxidised and converted into ferric oxide, while the sulphur is chiefly given off as sulphurous oxide. When very gradually heated some ferrous sulphide is formed, the residue having a composition represented by the formula 5FeS, Fe_2S_3. Ferric sulphide combines with alkaline sulphides, forming substances which are represented by the formulæ K_2S, Fe_2S_3 and Na_2S, Fe_2S_3; they may be prepared by melting a mixture of iron filings, sulphur and alkaline carbonate, and afterwards extracting the mass with water.

FERROSO-FERRIC SULPHIDE.

FORMULA FeS, Fe_2S_3. MOLECULAR WEIGHT 296.

This substance occurs naturally as one of the varieties of pyrrhotin or magnetic pyrites, or hepatic pyrites, which more frequently however has a composition corresponding with the formula $Fe_7S_8 = 5FeS.\ Fe_2S_3$. It is this latter substance which is obtained by heating the disulphide or ferric sulphide out of contact with air, and by heating iron filings with a slight excess of sulphur till the mass melts. Magnetic pyrites when crystalline presents a form belonging to the hexagonal system, but it is frequently compact, granular, or amorphous. The colour varies from bronze yellow to copper red; as prepared artificially it has a brownish-yellow colour. The specific gravity varies from 4·51 to 4·64. It is attracted by the magnet. When heated in a close vessel it is not altered; but in contact with atmospheric air it is oxidised, gives off sulphurous oxide, and is converted into ferric oxide. Heated in contact with hydrogen it yields sulphuretted hydrogen, and is converted into ferrous sulphide. It is dissolved by dilute acids with separation of sulphur, and sulphuretted hydrogen is given off.

IRON DISULPHIDE.

FORMULA FeS_2. MOLECULAR WEIGHT 120.

History.—The various kinds of pyrites occurring naturally were often confounded together by the ancients; and, even so late as the time of Agricola, copper pyrites and iron pyrites were regarded as being merely varieties of the same mineral.

Occurrence.—Iron disulphide occurs very abundantly as iron pyrites, of which

there are two distinct kinds differing in colour and crystalline form. Mundic or yellow iron pyrites crystallises in cubes or some other form belonging to the regular system; it also occurs in compact granular or fibrous masses; it is opaque, has a metallic lustre and a bronze yellow colour: the specific gravity varies from 4·98 to 5·1.

Marcasite or white iron pyrites crystallises in rhombic prisms, but occurs also in compact or granular masses; it has a pale yellowish grey colour and metallic lustre: the specific gravity varies from 4·65 to 4·85.

The following table gives the composition of several kinds of iron pyrites from different localities:

		Pattinson								Clapham
	FeS_2	Spain		Belgium	Westphalia	Norway	Ireland	Coalbrasses	Wales	Cornwall
Iron	46·63	38·70	41·41	39·68	38·22	39·22	40·52	31·44	49·72	32·20
Sulphur	53·33	44·60	49·30	45·01	45·60	45·50	44·20	38·10		34·34
Copper	—	3·80	5·81	—	—	1·80	0·90	trace	—	0·80
Lead	—	0·58	0·66	0·37	0·64	—	1·50	—	—	0·40
Zinc	—	0·30	trace	1·80	6·00	1·18	3·51	—	—	1·32
Thallium	—	trace	trace	trace	trace	—	—	—	—	—
Ferrous oxide	—	—	—	—	—	—	—	—	11·01	—
Lime	—	0·14	0·14	0·25	0·11	2·10	0·24	4·96	7·95	—
Magnesia	—	trace	trace	—	—	0·01	—	0·33	5·74	—
Carbonic acid	—	—	—	—	—	1·65	—	5·11	19·29	—
Arsenic	—	0·26	0·31	trace	trace	—	0·33	trace	—	0·91
Oxygen	—	0·23	0·25	0·42	0·37	0·45	0·25	0·31	—	—
Coaly substance	—	—	—	—	—	—	—	14·45	6·10	—
Gangue	—	11·10	2·00	12·23	8·70	9·08	8·80	1·40	—	29·0
Moisture	—	0·17	0·05	0·25	0·36	0·17	0·90	0·90	—	—
		99·88	99·93	100·01	100·00	101·16	101·15	97·00	99·81	98·97

Iron disulphide is decomposed when heated to redness in a close vessel, and by giving off three sevenths of its sulphur is converted into ferroso-ferric sulphide Fe_7S_8 according to the equation:

$$7FeS_2 - 6S = Fe_7S_8 \text{ or } 5FeS, Fe_2S_3.$$

When heated in contact with atmospheric air it burns with the blue flame of sulphur, and is gradually converted into ferric oxide, while sulphurous oxide is given off.

Yellow iron pyrites in a crystalline or compact state does not undergo alteration when exposed to the air, and the artificially prepared disulphide when compact is but slowly oxidised in the presence of moisture; but white iron pyrites is rapidly oxidised, and when the yellow variety is in a finely divided condition it is also oxidised by exposure to the air at ordinary temperatures with considerable evolution of heat. It is in this way that coal is sometimes ignited by the oxidation of iron pyrites, finely disseminated throughout its mass. The same alteration of iron pyrites by atmospheric oxygen takes place in the aluminous shale from which alum is made, and the pyrites is gradually converted into ferrous sulphate; sulphuric acid is also formed, which acts upon the aluminous silicate and forms aluminum sulphate (see p. 309). When iron pyrites is ignited with carbonaceous substances carbon bisulphide is formed; when mixed with 10 per cent. of charcoal and exposed to the action of superheated steam mixed with atmospheric air, the whole of the sulphur is said to be given off partly as sulphuretted hydrogen and sulphurous oxide, and partly in the free state, while the iron remains either in the metallic state or as ferric oxide.

FERROUS SULPHATE.

Formula $FeSO_4 7H_2O$. Molecular Weight 278.

Characters.—Ferrous sulphate forms pale bluish-green crystals, easily soluble in water; it has a ferruginous, astringent taste, and absorbs oxygen very readily, both in the dry state and in solution, with formation of basic ferric sulphate. The colour of commercial green vitriol is often dark green or greenish brown, owing to the presence of ferric salt.

For many purposes it is more advantageous to employ the pure salt, especially when other substances are to be reduced by it, as, for instance, in the reduction and solution of indigo, in the indigo vat. For other purposes, as in the preparation of a number of pigments, an impure salt containing basic ferric oxide is preferable.

On heating ferrous sulphate most of the water of crystallisation is expelled, but one molecule remains even at 260°C. At a higher temperature, it is decomposed as follows: $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$; but this reaction generally takes place in the presence of a little water, so that the distillate consists of a thick oily liquid, known as 'Nordhausen acid.' This name was derived from Nordhausen, at which place the sulphuric acid of commerce was made by the same method, long before the present mode of manufacture was introduced. The ferric oxide which remains after the distillation is sold under the name of colcothar, rouge or crocus of Mars, and is largely used for glass polishing and as a pigment.

Ferrous sulphate forms double combinations with the sulphates of the alkali metals, the potassium compound being $FeSO_4K_2SO_46H_2O$, and has the power of absorbing nitric oxide in common with other ferrous salts.

Preparation.—For preparing pure ferrous sulphate, iron is dissolved in dilute sulphuric acid, an excess of iron being necessary to prevent oxidation; the solution is then filtered quickly, rendered slightly acid by the addition of sulphuric acid, and evaporated to crystallisation. The addition of sulphuric acid to the filtered solution, before evaporating, is made for the purpose of dissolving up any basic ferric sulphate that may be formed by the action of the air upon ferrous sulphate during the evaporation. Crystals of ferrous sulphate, in order to keep well, must be perfectly dry, but the drying must be effected without the application of heat, owing to the readiness with which ferrous sulphate oxidises at a slightly elevated temperature. The best method of drying the crystals is to place them on a filter and wash them with alcohol. Ferrous sulphate thus prepared keeps much better than that prepared in the ordinary way. The reason is that the ferric sulphate is very soluble in alcohol, which dissolves out any trace of that salt; crystals that are free from ferric sulphate keep well, but the presence of a mere trace of ferric salt is sufficient to cause the whole mass to pass into the higher oxidised state.

Ferrous sulphate may be prepared in a very pure and finely divided state by precipitating a concentrated aqueous solution of the salt with alcohol, filtering and washing the precipitate with alcohol. Thus prepared the salt keeps well.

Ferrous sulphate is also prepared on a large scale by dissolving scrap iron with warm sulphuric acid, specific gravity of 1·150, in vessels lined with lead, and evaporating the neutral solution until a portion rapidly cooled deposits a sufficient quantity of solid salt. When this point has been attained the evaporation is stopped, the liquid left to settle, drawn off from the sediment into large tanks, where it is left for 24 hours to clear, and then the liquid is run into the crystallising vessels. In order to facilitate the formation of good crystals, pieces of string or straws are supported from pieces of wood laid across the crystallising vessels, so as to dip into the liquid, and crystals are deposited upon them. Sometimes pieces of wood are used in the place of string. When the crystallisation is complete, the mother liquor is drawn off, the crystals removed, washed with a small quantity of water, and dried. The crystals deposited on the sides of the vessels are separated from those formed in the midst of the solution, which are purer.

Large quantities of green vitriol are prepared from iron pyrites, partly as a by-product of the alum manufacture, and partly in the manufacture of sulphur by distillation from iron pyrites; it is also formed by partly roasting iron pyrites, and then exposing it to the action of the atmosphere.

When the iron pyrites contained in alum slate is oxidised by roasting or weathering, ferrous sulphate is formed, together with sulphuric acid and sometimes also sulphurous acid. Upon lixiviating the oxidised mass, ferrous sulphate is dissolved, and separated either before precipitation of the alum, or afterwards by crystallisation from the mother liquor.

In some districts sulphur is obtained by distillation from iron pyrites, the disulphide of iron being converted into sulphur and ferrous sulphide, which remains in the retort.

This residue, termed sulphur waste, is taken out and laid upon shelves slightly inclined, where it is allowed to remain for some time in contact with the air, and by oxidation is converted into ferrous sulphate:

$$FeS + 4O = FeSO_4.$$

Upon lixiviating the weathered mass at intervals, the ferrous sulphate dissolves out and is obtained in the crystalline form by evaporating the solution. In some

districts the lixiviation is effected by rain, the solution thus formed being collected in a large reservoir placed beneath the heap.

Ferrous sulphate is also obtained by the weathering and lixiviation of the pyrites often found in large quantities in both brown coal and ordinary coal.

At Fahlun ferrous sulphate is obtained as a by-product of the extraction of copper from mine water containing cupric sulphate, copper being precipitated in the metallic state by means of iron, while ferrous sulphate is formed, and can be obtained by evaporating the liquid.

Ferrous sulphate is also obtained as a by-product in the preparation of sulphuretted hydrogen, which is used in large quantities in some sulphuric acid works for precipitating arsenic (vide page 137):

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The solution thus obtained, containing ferrous sulphate, is evaporated to a specific gravity of 1·357, and then left to crystallise.

Uses.—One of the chief uses of ferrous sulphate is in dyeing textile tissues, leather, wood, etc., for various black, grey, lilac, and brown shades. These colours, as well as the preparation of ordinary writing-ink, are due to the formation of compounds of the iron and salt with organic substances. Ferrous sulphate is also used as a mordant for producing Prussian blue in calico printing. After conversion into basic ferric salt, by oxidation, it is used in the preparation of Nordhausen sulphuric for dissolving indigo. A weak aqueous solution of ferrous sulphate is said to be useful in preventing the chlorosis of plants. Mixed with excremental matter, ferrous sulphate converts the bad smelling volatile substances into non-volatile compounds, and thus serves as a deodoriser; besides which, it retains volatile ammonium compounds, such as ammonium carbonate and ammonium sulphide, by converting them into ammonium sulphate.

Preparation of Ink.—By mixing a ferric salt with a solution containing tannin, such as a decoction of nutgalls, oak bark, or similar substances, a black liquid is produced, which results from the formation of ferric tannate, that is suspended in the water in a very fine state of division, and is only gradually deposited as a black precipitate. When a solution of ferrous sulphate is used, the black coloration is gradually produced in proportion as air is allowed to mix with the solution and oxidise the ferrous sulphate.

When a liquid prepared as above is mixed with some mucilaginous substance such as gum arabic, the ferric tannate remains for the greater part permanently suspended, and ordinary writing ink is a liquid of this kind.

Recipes for preparing ink are numerous enough. The best ferruginous inks are prepared with nutgalls; the following recipe may serve as an illustration:

Broken nutgalls	2 parts by weight.
Ferrous sulphate	1 part „
Logwood chips	0·15 „ „
Gum arabic	1·2 „ „
River water	22 parts „
Oil of lavender	a few drops.

The galls and logwood chips are macerated for 24 or 36 hours in 10 or 51 parts of water, and then boiled for 2 hours, water being added in proportion as it evaporates; the decoction is then strained through a cloth and mixed with the gum arabic and ferrous sulphate, each previously dissolved in 2 or 3 litres of water. The mixture is then exposed in shallow vessels for 2 or 3 days to the action of the atmosphere, with frequent stirring, so as to oxidise the ferrous salt as completely as possible; lastly, the oil of lavender is added, and the ink preserved for use in well-closed bottles.

Ink is generally pale at first, and darkens upon drying on the paper in proportion as ferric salt is formed. When a ferric salt is employed in the preparation, the ink does not flow readily from the pen. Ink of this kind when dry is insoluble in water, but easily soluble in dilute hydrochloric or sulphuric acid. Chlorine at once destroys its colour.

A still better ink is said to be obtained as follows: 4 parts by weight of nutgalls are covered with 22 parts by weight of water, and allowed to remain 2 days under frequent stirring; the nutgalls are then pressed, and the liquid exposed in summer for two months to the action of the atmosphere. To the mass, which is then covered with mould, is added 2 parts of ferrous sulphate and 1 part of gum arabic, both in a state of solution, so that the entire quantity of ink amounts to 22 parts. Ink thus prepared contains ferrous gallotannate, which is black, but does not deposit; another excellent feature of this ink is that it does not become mouldy.

A very cheap kind of ink, which does not attack steel pens, flows well from the pen, writes at once black, does not become mouldy, and is not dissolved by dilute acids like ordinary ink, may be prepared by boiling 125 parts of logwood in sufficient water to form a decoction of 1,000 parts, and adding when cold 1 part of yellow potassium chromate. The ink thus obtained is bluish black, forms no deposit, flows well from the pen without any addition of gum, and has the great advantage of being extremely cheap.

Sulphate of copper may also be substituted with advantage for sulphate of iron in logwood inks. The following is the formula for such an ink, given in proportions for a manufacturing scale: 20 parts by weight of extract of logwood are dissolved in 200 parts of water, and the liquor clarified by subsidence and decantation. A yellowish-brown liquid is thus obtained. In another vessel 10 parts of ammonia-alum are dissolved in 20 parts of boiling water. The two solutions are mixed, 0·2 part by weight of sulphuric acid is added, and finally 1·5 part of sulphate of copper. The ink should be exposed to the air for a few days to acquire a good colour, after which it should be stored in well-corked bottles.

Alizarin Ink.—This ink flows well from the pen, and does not form any deposit. Winternitz describes its preparation as follows: 100 parts of nutgalls are digested with 1,200 parts crude wood vinegar for several days, the liquid filtered off and the nutgalls washed upon the filter with a quantity of wood vinegar sufficient to make up 1,200 parts. In this liquid is then dissolved 12 parts ferrous sulphate and 50 parts gum arabic, indigo carmine being added until the entire quantity of liquid amounts to 1,500 parts.

Leonhardi's recipe recommends, for preparing alizarin ink, extracting 42 parts nutgalls and 3 parts madder with hot water, sufficient to form 120 parts of solution, filtering and adding 1·2 part of indigo solution. This ink admits of being dried and transported in the dry state, 1 part of the dry ink requiring for solution 6 parts of water.

Copying Ink.—This consists in most cases of ordinary ink to which a considerable quantity of sugar or gum has been added.

Red Ink.—Boothe's method of preparing red ink consists in boiling together 2 ounces of brazil-wood chips with ½ drachm salt of tin, and 1 drachm gum arabic with 32 ounces of water. The whole is boiled until the net weight amounts to 16 ounces; the red liquor is then filtered off.

Other kinds of red ink are prepared from cochineal, or carmine, generally dissolved by the aid of a solution of ammonia.

Blue Ink.—Normandy's is made by triturating together 1 drachm salt of sorrel, 3 drachms Prussian blue, 7 ounces of water, and 1 drachm gum arabic. Nearly all kinds of blue ink owe their colour to Prussian blue.

FERRIC SULPHATE.

Formula $Fe_2 3SO_4$. Molecular Weight 400.

This salt is found native in considerable quantities in Chili as coquimbite, as a white silky mineral or as powder $Fe_2 3SO_4 9H_2O$. It is best prepared artificially by mixing ferrous sulphate with sulphuric acid in the proportions so as to bring up the relation of the one to the other to that form in which they exist in ferric sulphate; the mixture is then boiled and peroxidised by the addition of nitric acid. When the solution obtained in this way is evaporated sufficiently, a buff coloured mass is obtained, which is not very soluble in water; at a gentle heat the salt is rendered anhydrous.

With the sulphates of potassium and ammonium, ferric sulphate forms compounds of the form and constitution of alums; thus we have

$$K_2Fe_24SO_424H_2O, \quad \text{and} \quad 2NH_4.Fe_24SO_424H_2O.$$

Several basic sulphates of iron are known.

FERROUS CARBONATE.

Formula $FeCO_3$. Molecular Weight 116.

This substance occurs in nature as spathose iron ore or iron spar in immense quantities, forming a most valuable ore of iron; in its less usual condition it exists in a highly crystalline form isomorphous with calc spar. Clay iron ore is another impure form of ferrous carbonate.

Ferrous carbonate exists in many mineral waters, being held in solution by the excess of carbonic anhydride; such waters deposit ferric oxide on exposure and standing.

When ferrous carbonate is strongly heated in a closed vessel, carbonic anhydride and carbonic oxide are evolved, and magnetic oxide remains behind.

$$3FeCO_3 = Fe_3O_4 + 2CO_2 + CO.$$

Ferrous carbonate may be produced by precipitating ferrous salts with an alkaline carbonate, and in this state it constitutes a whitish-green precipitate which rapidly undergoes atmospheric oxidation, losing carbonic anhydride and becoming hydrated ferric oxide.

METALLURGY OF IRON.

Iron is always obtained in the metallic state by the reduction of one of the oxides, by heating either in contact with hydrogen gas, carbon, carbonic oxide, or some other substance capable of combining with oxygen. When this reaction takes place at a moderate temperature the metal is obtained in a finely divided pulverulent condition; in this state it is pyrophoric and takes fire on contact with atmospheric air, being converted into ferric oxide or magnetic oxide. When the reduction is effected at a full red heat, the metal is obtained in a partially coherent state, forming a porous spongy mass which is less readily oxidised.

Owing to the high melting point of pure iron, it is difficult to obtain the metal in a compact state; but when metallic iron is intensely heated in contact with carbon or carburetted gases, it combines with the carbon, and is then fusible at a much lower temperature than pure iron. Since carbon is the reducing agent employed in smelting iron ores, the metal obtained in this operation always contains some carbon, and from its consequent greater fusibility in that state this circumstance is an important means of facilitating the manipulation of the metal. As already mentioned, the degree of fusibility of carburetted iron depends upon the proportion of carbon in the metal, and when this amounts to from 3 to 6 per cent., the metal is sufficiently fusible to be run out from the smelting furnace in a liquid state and cast in moulds. In the extraction of iron from such of its ores as are suitable for metallurgic purposes, and as that operation is now chiefly carried out in iron-producing countries, the metal is always obtained in the first instance in the carburetted state, commonly known as crude iron or pig iron, on account of its being run out from the smelting furnace into ingot-shaped masses.

The processes comprised in the smelting of iron ores by this method are:

1. The separation of water, carbonic acid, sulphur, and other volatilisable substances by the action of the heat upon the ore, so as to bring it as nearly as possible to the condition of ferric oxide or magnetic oxide.

2. The reduction of the oxide thus prepared to the metallic state by the action of carbonic oxide under the influence of heat.

3. The separation of the earthy substances commonly present in iron ores, from the reduced metal, by the formation of compounds of those substances which are fusible at a high temperature, as slag.

4. The carburation and melting of the reduced metal.

The operations by which iron ores are brought to a condition fit for being smelted vary according to the nature of the ore worked. In most instances the preparation of the ore is effected by roasting, and sometimes this treatment is preceded by a mechanical operation of washing. The only ferruginous minerals that are suitable for the extraction of iron are the several oxides and the carbonate, all of which occur naturally in great abundance, but associated with varying proportions of silicious or earthy minerals and other admixtures in smaller amount.

The most important varieties of iron ore are the following:

Magnetic Iron Ore.—This mineral consists essentially of magnetic oxide of iron and is known by the name of magnetite; when pure it is the richest of all the iron ores, containing upwards of 72 per cent. of iron. It is black and generally has a metallic lustre, occurring both crystalline or granular and compact, or even earthy, as well as in the state of sand. In many localities it forms beds or veins, and sometimes enters mountain masses associated with volcanic or schistose rocks, chiefly in Norway, Sweden, Siberia and North America, to some extent also in the west of England, and at Rosedale, in Yorkshire. This ore is sometimes largely mixed with pyrites and other sulphuretted minerals. The mineral known as Franklinite appears to be a variety of magnetic iron ore in which ferrous oxide is replaced by zinc oxide.

Analyses of Magnetic Iron Ore.

	Dartmoor	Cornwall		Rosedale		Dannemora	Franklinite
	Riley	Noad		Northcutt	Pattinson	Karsten	Rammelsberg
Ferric oxide	62·20	44·40	66·50	12·22	32·67	70·23	64·51
Ferrous oxide	17·32	20·00	13·00	35·25	33·85	29·65	—
Manganous oxide	·14	·16	·56	—	·69	—	13·51
Zinc oxide	—	—	—	—	—	—	25·30
Alumina	3·81	5·20	3·60	14·10	3·15	—	—
Lime	5·52	·60	·56	2·38	2·86	—	—
Magnesia	1·82	1·00	1·52	3·95	1·59	—	—
Potash and soda	·10	—	—	—	trace	—	—
Silica	9·66	—	—	9·65	6·95	—	—
Carbonic acid	—	—	—	16·25	10·36	—	—
Phosphoric acid	·10	·50	·57	—	1·41	—	—
Sulphuric acid	—	·04	·04	trace	trace	—	—
Iron pyrites	·07	—	—	trace	·03	—	—
Water combined	·28	2·50	3·20	4·80	3·76	—	—
Water hygroscopic	·34						
Insoluble in acid	—	24·20	9·40	—	·84	—	—
	101·36	98·60	98·95	98·60	98·16	99·88	103·32
Percentage of iron	57·01	–	—	35·98	49·17	71·68	45·16

Hematite, or red iron ore.—This mineral consists essentially of ferric oxide and in the purest state contains 70 per cent. of iron. It occurs in various states, crystalline, massive, compact and earthy; very often the lumps of ore have a radiating, fibrous structure and smooth nodular surface; in this form it is known as kidney ore. Hematite also forms large veins or beds associated with quartz, calcspar and heavy spar. Some kinds of the ore are hard, others soft and friable, and it generally contains a varying amount of earthy admixtures. The principal deposits of hematite in Great Britain are in Cumberland, Lancashire, the Isle of Man, Devonshire and Cornwall. On the Continent it occurs chiefly in the Hartz, Silesia, Austria and Norway. A peculiar oolitic hematite occurs in the neighbourhood of Liége. Red ochre is an earthy variety of ferric oxide containing a large proportion of clay.

Analyses of Red Iron Ore.

	Whitehaven		Ulverstone		Cleator	Ulverstone	Whitchurch
	Dick		Spiller	Smith	Dick		Ratcliffe
Ferric oxide	98·71	95·16	94·23	90·94	90·55	86·5	66·55
Ferrous oxide	—	—	—	—	—	—	1·13
Manganous oxide	trace	·24	·23	·25	·10	·21	1·13
Alumina	—	·06	·63	trace	1·43	·30	2·79
Lime	trace	·07	·05	·99	·71	2·77	9·40
Magnesia	—	—	trace	trace	·06	1·46	1·39
Potash	—	—	—	—	—	—	·42
Soda	—	—	—	—	—	—	·15
Silica	1·00	5·66	4·90	6·68	7·05	6·18	8·90
Carbonic acid	—	—	—	·78	—	2·96	5·73
Phosphoric acid	trace	trace	trace	trace	trace	trace	1·02
Sulphuric acid	—	trace	—	·24	trace	·11	1·31
Iron pyrites	—	trace	·09	—	—	—	—
Water combined	—	—	·03	—	—	—	—
„ hygroscopic	—	—	·17	—	—	—	2·12
Organic substance	—	—	·39	—	—	—	·38
	99·71	101·19	100·72	99·88	99·90	100·49	102·42
Percentage of iron	69·10	66·60	65·98	63·66	63·25	6·55	47·47

Specular iron ore also consists of anhydrous ferric oxide in a crystallised state. Its colour varies from iron grey to black. Specific gravity 4·8 to 5·3. The crystals of this mineral belong to the hexagonal system. Specular iron ore occurs chiefly in schistose rocks, in Norway, the Erzgebirge, Russia, and several parts of the south of Europe, the most extensive deposit being in the island of Elba, where it has been worked for upwards of 3,000 years. This mineral often contains titanic oxide, either in the form of rutile, or combined with the ferric oxide constituting ilmenite. The presence of this substance was formerly considered prejudicial to the ore, but more recently it has been stated that the presence of titanium in iron ores contributes, in some way not yet understood, to the production of good iron.

Brown iron ore consists essentially of hydrated ferric oxide, and is sometimes called brown hematite. In the pure state it contains 59·89 per cent. of iron and 14·44 per cent. of combined water. It is sometimes indistinctly crystalline or fibrous; but more generally compact or earthy, and of various shades of colour from blackish-brown to yellowish-brown. This ore frequently contains a considerable amount of manganese oxides, together with a varying proportion of earthy admixtures. It occurs abundantly in the Forest of Dean in Gloucestershire, in several parts of Devonshire, Northamptonshire and Lincolnshire, as well as in Weardale, Durham, where it has originated chiefly by the alteration of spathic iron ore. On the Continent it is very abundant, and it is one of the principal ores smelted in France. A very large deposit of this ore occurs in the carboniferous limestone in the neighbourhood of Bilbao in Spain. The mine of Somorrostro is very extensively worked, and is said to yield as much as 1,000 tons of ore daily. At the Galdames mine there is a mountain, consisting entirely of iron ore, 1,200 yards long, and rising about 170 yards high above the river. The quantity of ore actually in sight is estimated at from sixty to seventy million tons, and it is believed that there is three or four times that quantity of ore to be obtained at this place.

Brown hematite also occurs in lias, oolite, and greensand rocks of more recent date than the coal measures, but then it is often less pure than the ore found in older rocks, which is frequently a product of the oxidation of ferrous carbonate.

A variety of brown iron ore known under the name of bog iron ore occurs in many places, and it has probably been formed by deposition from ferruginous water under the influence of living organisms. Some kinds of this ore furnish very good iron, as for instance the lake ores of Sweden and Lower Canada, but generally the amount of phosphates in bog iron ore is so large as to render it useless for the production of malleable iron.

Yellow ochre is an argillaceous variety of hydrated ferric oxide, containing more combined water than brown iron ore, together with basic ferric sulphate and sometimes also silicate, phosphate, or arsenate.

Analyses of Brown Iron Ore.

	Dean Forest			Devonshire	Northamptonshire		Weardale	
	Price	Dick	—	Dick	—	—	Tookey	Spiller
Ferric oxide	89·28	90·05	89·80	89·39	76·00	74·32	72·08	49·57
Ferrous oxide	—	—	—	—	trace	—	—	10·77
Manganous oxide	—	·88	·04	·33	·40	·57	6·60	3·06
Alumina	—	·14	·98	·52	2·30	2·91	·40	·84
Lime	—	·06	·51	·33	·41	·76	·56	5·69
Magnesia	—	·20	·40	·20	·11	·18	1·90	1·21
Potash	—	—	—	—	—	—	—	·05
Silica	·98	·92	2·14	1·42	5·33	6·03	4·09	6·64
Carbonic acid	—	—	—	—	—	·57	·13	14·49
Phosphoric oxide	trace	·09	·13	·13	1·03	3·17	·22	·01
Sulphuric oxide	—	trace	trace	trace	—	trace	—	trace
Iron pyrites	—	trace	—	trace	—	·06	—	·03
Water combined	9·74	9·22	7·05	8·83	12·40	11·89	12·40	6·63
Water hygroscopic		—	—		1·80	—		1·81
Organic substance	—	—	—	—	—	trace	—	trace
	100·	101·56	101·05	101·15	99·78	100·46	99·38	100·80
Percentage of iron	62·57	63·04	62·86	62·60	53·20	52·05	49·78	43·02

Analyses of Brown Iron Ore—continued.

	Northampton-shire	Wales: Llantrissant	Lincoln-shire: Brigg	Northampton-shire	Dorset-shire	Wilt-shire: Seend	Northampton-shire	Corn-wall: St. Austell
	Price and Nicholson	Riley	Tookey	Percy	Tookey	Riley	Spiller	Riley
Ferric oxide	68·58	59·05	58·10	56·20	55·21	53·48	52·86	51·87
Ferrous oxide	—	—	—	trace	—	—	trace	—
Manganous oxide	0·36	0·09	0·88	0·20	0·95	1·60	0·51	0·43
Alumina	3·27	trace	4·95	2·43	7·70	4·38	7·39	4·01
Lime	0·66	0·25	4·15	0·49	0·70	0·84	7·46	0·52
Magnesia	—	0·28	0·96	0·17	1·15	0·72	0·68	0·17
Silica	11·63	34·40	11·70	29·07	19·65	26·23	13·16	36·03
Carbonic acid	—	—	1·08	—	—	trace	4·92	—
Phosphoric acid	0·97	0·14	1·40	0·84	0·42	0·87	1·26	0·49
Sulphuric acid	0·18	—	—	—	0·16	—	—	—
Iron pyrites	—	0·09	—	—	—	trace	0·03	0·03
Water (hygroscopic)	11·56	0·24	16·46	1·16	13·11	13·61	—	0·80
Water (combined)		6·14		9·74			11·37	5·80
Organic substance	—	—	—	—	—	—	—	—
	97·21	100·68	99·68	100·30	99·05	101·73	99·64	100·15
Percentage of iron	48·00	41·34	40·67	39·34	38·65	37·44	37·00	36·31

	Northampton-shire	Oxfordshire: Woodstock	Dean Forest	Staffordshire: Froghall	Northampton-shire	Dean Forest	Belfast	Northampton-shire
	Dick	Tookey	Dick		Riley	Dick	Tookey	Riley
Ferric oxide	38·04	44·67	32·76	52·83	50·53	48·99	35·91	34·41
Ferrous oxide	10·54	0·86	—	—	trace	0·24	6·57	trace
Manganous oxide	0·69	0·44	trace	0·81	0·51	0·16	0·05	0·27
Alumina	13·02	9·10	0·05	—	7·52	0·17	27·95	6·40
Lime	trace	9·29	0·25	14·61	11·92	14·07	0·60	25·72
Magnesia	4·35	0·66	0·25	5·70	0·62	10·21	0·20	0·87
Potash	0·38	—	—	—	0·11	—	0·49	—
Silica	23·24	12·34	63·52	trace	8·80	0·79	9·75	6·69
Carbonic acid	0·16	6·11	—	18·14	7·98	20·75	—	18·45
Phosphoric acid	0·26	0·55	0·09	0·32	1·28	0·06	—	1·47
Sulphuric acid	trace	—	trace	0·28	—	trace	—	0·07
Iron pyrites	0·13	trace		—	0·17	—	—	0·30
Water (hygroscopic)	—	16·31	—	—	11·00	—	18·60	6·97
Water (combined)	6·92		3·55	4·75		5·18		
Organic substance	0·19	—	—	1·30	—	—	—	—
	97·92	100·33	100·47	98·74	100·44	100·62	100·12	101·62
Percentage of iron	34·83	31·94	22·93	36·98	35·37	34·46	30·25	24·09

Spathic iron ore consists essentially of ferrous carbonate, and in its purest state it contains 48·27 per cent. of iron. It is generally crystalline, sometimes presenting distinct crystals; it also occurs in the form of fibrous nodular masses known by the name of sphærosiderite. It varies in colour from white to yellow or brown, and is very often found to have undergone partial conversion into hydrated ferric oxide. Spathic iron ore occurs as veins or beds in the older rocks and associated with limestone strata; it frequently contains manganous carbonate, calcic carbonate, or magnesic carbonate, and is sometimes associated with lead or copper ore, quartz, fluor spar, calc spar, heavy spar, etc. It is worked in this country chiefly in Durham and Somersetshire;

on the Continent it occurs more frequently and in great abundance, the chief localities being Styria and Westphalia, where it constitutes entire mountains, and has long been renowned under the name of steel ore for yielding very fine qualities of iron and steel.

Analyses of Spathic Iron Ore.

	Westphalia: Müsen	Durham: Ripsey vein	Durham: Weardale	Somersetshire: Brandon		Siegen	Saxony	Devon: Exmoor
	Peters	Dick	Tookey	Spiller	Price and Nicholson	Schnabel	Magnus	Spiller
Ferric oxide	2·75	—	0·81	0·81	—	—	—	0·07
Ferrous oxide	48·13	49·47	49·77	43·84	43·94	43·59	36·81	17·91
Manganous oxide	0·83	2·42	1·93	12·64	12·88	17·87	25·31	7·64
Zinc oxide	0·04	—	—	—	—	—	—	—
Alumina	1·63	0·06	—	0·01	—	—	—	—
Lime	1·75	3·47	3·96	0·28	—	0·88	—	24·80
Magnesia	2·29	3·15	2·83	3·63	4·00	0·24	—	6·17
Silica	1·62	4·93	3·12	0·07	—	—	—	—
Carbonic acid	39·92	37·71	37·20	38·86	39·18	38·22	38·35	41·75
Phosphoric acid	0·54	trace	trace	—	—	—	—	trace
Sulphuric acid	—	trace	—	—	—	—	—	—
Iron pyrites	0·22	—	0·04	—	—	—	—	0·11
Water hygroscopic	—	—	0·30	0·18	—	—	—	0·38
Water combined	0·45	—	—	—	—	—	—	—
Organic substance	0·39	trace	—	—	—	—	—	—
	100·55	101·21	99·96	100·32	100·00	100·20	100·47	98·83
Percentage of iron	42·59	38·56	38·95	34·67	34·18	33·90	28·03	13·98

Ferrous carbonate mixed with clay often occurs with beds of coal in sedimentary rocks, and is then known under the name of clay iron ore or argillaceous sphærosiderite. This ore occurs in lenticular masses or nodules; it is compact and earthy,

Analyses of Clay Iron Ore from the Coal Measures.

	Lowmoor	Parkgate		Butterley	Stanton	Staveley	Staffordshire	
	Spiller						Dick	
Ferric oxide	1·45	1·69	2·39	1·49	3·49	1·42	0·12	0·05
Ferrous oxide	36·14	39·38	41·77	37·99	39·55	28·27	51·07	46·53
Manganous oxide	1·38	0·95	1·13	1·51	1·50	1·02	2·36	2·54
Alumina	6·74	6·42	4·79	5·57	5·45	2·21	2·47	1·22
Lime	2·70	2·26	2·55	4·59	3·38	13·94	1·74	2·44
Magnesia	2·17	3·89	3·85	3·37	2·88	9·27	1·10	1·39
Potash	0·65	0·37	0·43	0·55	0·48	0·16	0·28	0·20
Silica	17·37	12·16	8·93	10·04	10·22	3·55	3·02	1·93
Carbonic acid	26·57	29·38	31·39	29·92	28·63	37·61	33·63	30·77
Phosphoric acid	0·34	0·47	0·75	0·80	1·12	0·74	1·12	0·69
Sulphuric acid	trace	—	trace	trace	trace	trace	trace	0·04
Iron pyrites	0·10	trace	—	0·06	0·05	0·04	0·17	0·34
Water hygroscopic	0·61	0·68	0·55	0·74	0·51	0·18	0·99	1·47
Water combined	1·16	1·41	1·15	1·47	1·24	0·73		
Organic substance	2·40	0·54	0·86	1·42	1·14	0·92	1·24	10·46
	99·78	99·60	100·54	99·52	99·64	100·06	99·01	100·07
Percentage of iron	29·12	31·82	34·16	30·60	33·20	22·98	39·88	36·39

of various shades of grey or brown, and sometimes it is quite black, owing to the admixture of carbonaceous material. Clay iron ore is generally very abundant in the coal

measures, but in some instances it is almost wholly wanting in those rocks; as, for instance, in the coal fields of Northumberland, Durham, Lancashire and Belgium. The principal localities where it is worked in this country are the coal fields of Scotland, Staffordshire, Shropshire and Wales. Clay iron ore is found abundantly in America, and also to some extent in France and Germany.

	Pins	Grains	Gubbin	White-stone	Binds	Balls	White-stone	Gubbin
	Dick			Spiller		Dick	Tookey	
Ferric oxide	0·54	0·13	0·40	0·04	1·15	0·43	3·17	3·82
Ferrous oxide	45·35	46·30	45·86	48·63	30·96	52·04	33·92	49·40
Manganous oxide	0·56	1·44	0·96	1·29	0·73	0·92	0·77	0·86
Alumina	5·70	4·80	5·86	3·64	9·58	4·98	6·44	3·05
Lime	2·60	0·76	1·37	4·45	1·84	0·53	2·65	0·86
Magnesia	1·26	0·94	1·85	0·80	3·11	1·18	4·43	0·52
Potash	0·36	—	—	0·11	0·74	0·32	0·74	0·30
Silica	10·63	10·29	10·88	6·21	26·50	6·63	18·23	6·22
Carbonic acid	30·21	30·44	31·02	32·16	22·13	32·31	26·89	32·05
Phosphoric acid	0·46	0·74	0·21	0·31	0·26	0·21	0·35	0·23
Sulphuric acid	trace	trace	trace	0·06	trace	trace	—	—
Zinc sulphide	—	—	—	—	—	—	—	1·27
Iron pyrites	0·20	0·07	0·10	0·16	0·12	0·13	0·15	0·13
Water (hygroscopic)	1·64	1·38	1·08	0·32	0·56	0·46	0·42	0·37
Water (combined)				1·23	1·83		0·98	0·29
Organic substance	1·59	1·14	0·90	0·28	0·10	0·51	0·47	0·54
	101·10	98·43	100·09	99·69	99·61	100·65	99·61	99·91
Percentage of iron	35·74	36·14	35·99	37·45	24·88	40·84	28·87	41·60

	Ponty-pool	Blae-navon	Car-narvon	Aberdare		Aber-carn	Llanelly	
	Balls	Black pin	Sul-phury mine	Coal brass		Blackband		
	Riley	Dick		Price and Nicholson		Rat-cliffe	Price	
							raw	calcined
Ferric oxide	0·50	0·45	0·34	—	—	4·10	—	80·00
Ferrous oxide	44·50	41·22	40·30	37·07	42·64	43·37	43·30	—
Manganous oxide	0·73	1·07	1·03	0·23	0·26	1·50	1·08	1·80
Manganic oxide	—	—	—	—	—		—	
Alumina	5·95	4·88	7·90	—	—	6·50	—	—
Lime	2·05	2·89	1·44	6·61	5·24	3·00	1·26	2·10
Magnesia	3·26	3·68	2·94	7·40	5·26	0·25	2·67	4·45
Soda	0·13	—	—	—	—	—	—	—
Potash	—	0·48	0·82	—	—	0·32	—	—
Silica	10·81	11·60	14·43	—	—	0·80	7·20	10·61
Carbonic acid	30·92	30·07	28·23	37·14	36·89	30·50	28·46	—
Phosphoric acid	0·23	0·76	—	0·23	0·17	trace	0·67	1·03
Sulphuric acid	—	trace	trace	—	—	—	—	—
Sulphur	—	—	—	—	—	1·56	0·26	—
Iron pyrites	0·11	0·15	0·09	trace	0·22	—	—	—
Clay	—	—	—	2·70	—	—	—	—
Water (hygroscopic)	0·76	—	0·74	—	—	0·27	—	—
Water (combined)		1·21	—	—	—	0·31	—	—
Organic substance	0·21	0·82	0·29	9·80	8·87	6·25	15·10	—
	100·16	99·28	98·55	101·18	99·55	98·73	100·00	99·99
Percentage of iron	34·96	32·44	31·63	28·88	33·17	36·4	33·68	56·00

A variety of clay iron ore known as black band, and containing from 10 to 15 or 20 per cent. of coaly substance, occurs as thin layers in the coal measures of Scotland and some parts of England and Wales.

	Scotch Blackband							
	Colquhoun							
Ferric oxide	—	0·33	1·16	0·23	0·47	1·16	0·23	2·72
Ferrous oxide	45·84	38·80	35·22	53·03	43·73	35·22	53·82	40·77
Manganous oxide	0·20	0·07	—	—	—	—	—	—
Alumina	2·53	6·20	5·34	0·63	5·13	5·34	—	—
Lime	1·90	5·30	8·62	3·38	2·10	8·62	1·51	0·90
Magnesia	5·90	6·70	5·19	1·77	2·77	5·19	0·28	0·72
Silica	7·83	10·87	9·56	1·40	9·70	9·56	2·00	10·10
Carbonic acid	33·63	30·76	32·53	35·17	32·24	32·53	34·39	26·41
Sulphur	—	0·16	0·62	—	0·20	0·62	—	—
Water hygroscopic	—	—	—	—	—	—	—	—
Water combined	—	—	—	—	—	—	—	1·00
Organic substance	1·86	1·87	2·13	3·63	1·50	2·13	7·70	17·38
	99·29	99·26	100·37	—	97·84	100·37	100·03	100·00
Percentage of iron	28·40	30·00	28·40	40·90	34·00	28·40	41·60	34·60

Clay iron ore also occurs abundantly in strata belonging to the Lias series, as well as the oolitic and tertiary series of rocks; sometimes it is partially or wholly converted into brown iron ore by atmospheric oxidation. This kind of ore is now worked on a large scale in the Cleveland district in Yorkshire.

	Middlesboro'	Hutton Low Cross	Eston Nab	Upleatham	Belmont	Grosmont	Normanby	Northamptonshire
	Percy	Crowder			Percy	—	Pattinson	Dick
Ferric oxide	2·86	4·25	1·20	5·80	3·50	—	2·60	3·31
Ferrous oxide	43·02	40·86	40·35	38·25	39·00	40·77	38·06	33·29
Manganous oxide	0·40	—	—	—	1·30	0·67	0 74	1·11
Alumina	5·87	3·44	9·88	12·20	7·46	1·32	5·92	7·89
Zinc oxide	5·14	3·80	0·58	5·00	7·44	4·08	7·77	0·50
Magnesia	5·21	3·70	5·35	2·40	3·82	5·34	4·16	11·77
Potash	—	—	—	—	—	—	—	0·20
Silica	7·17	7·20	7·65	7·45	9·46	8·80	10·36	19·49
Carbonic acid	25·50	32·50	22·96	25·40	23·06	31·80	22·00	24·79
Phosphoric acid	1·81	0·96	3·87	0·50	1·60	0·06	1·07	0·22
Sulphuric acid	—	0·30	—	trace	—	—	trace	trace
Iron pyrites	—	1·60	0·09	trace	—	—	0·14	0 13
Water hygroscopic	0·34	1·45	5·07	3·00	3·66	2·70	4·45	—
Water combined	3·14							·54
Organic substance	0·15	—	—	—	—	—	—	0·08
	100·61	100·06	100·00	100·00	100·30	95·54	97·27	103·32
Percentage of iron	35·46	34·75	34·54	38·81	32·78	31·71	31·42	18·28

The various kinds of argillaceous iron ore are frequently accompanied by other minerals, either metalliferous, sulphuretted, arsenical, or phosphatic, and the proportion of such admixtures is sometimes so large as to detract from the value of the ore for iron smelting; but, generally speaking, argillaceous iron ore is sufficiently pure to furnish iron of good quality.

The mechanical treatment to which iron ore is subjected before being smelted is generally more simple than in the case with other ores. In this country it is rarely

requisite to do more than break the masses of ore into lumps of tolerably uniform size in order to secure the regular working of the smelting furnaces.

With poor argillaceous brown iron ore, such as is used in many Continental districts for iron smelting, it is necessary to separate the adhering sand and clay by a preliminary operation of crushing and washing. A simple washing arrangement is to allow a current of water to pass through the ore, which is kept agitated in a cylindrical trough by means of a revolving horizontal shaft provided with paddles. In this way the clean ore is deposited, whilst the lighter earthy material is carried away in a fine state of division suspended in the water that runs off.

With some kinds of iron ore it is found often advantageous to expose them to the action of atmospheric air, by which they undergo oxidation and other changes. This is termed weathering, and in this way the shale adhering to such ores as the argillaceous ores of the coal measures becomes disintegrated and easily detached; in like manner the sulphuretted minerals—*e.g.* copper, iron, and magnetic pyrites—are oxidised and give rise to soluble sulphates which can be removed by washing with water. In addition to the removal of the sulphur, the iron becomes peroxidised and the mass is rendered much more porous. It is important when weathering ores to stop the action when it has advanced far enough for the object desired, so as to avoid unnecessary disintegration.

Iron ore is seldom smelted in a raw state, but is generally roasted beforehand. The chemical changes effected by calcination over and above the disintegration of the ore consist chiefly in the separation of water, carbonic acid, and bituminous material when the ore is carbonaceous. In this case the ferric oxide may undergo partial reduction to magnetic oxide or ferrous oxide; but more generally the effect of calcination is to bring the iron into the state of ferric oxide, if it be not already in that condition. Another important effect of calcination is the removal of sulphur, which is in most instances present in the state of pyrites. By the action of heat this is decomposed, losing half of its sulphur, and the residual ferrous sulphide is then converted by oxidation into sulphate which may be decomposed if the heat applied in roasting the ore be sufficient. However, the entire separation of sulphur in this way is rarely practicable.

The following analyses of Cleveland iron ore in the raw state and after calcination will serve to illustrate the nature of the change produced by roasting:

	Raw	Calcined
Ferrous oxide	38·06	—
Ferric oxide	2·60	66·25
Manganous oxide	·74	—
Mn_3O_4	—	·65
Alumina	5·92	7·72
Lime	7·77	6·46
Magnesia	4·16	4·78
Potash	trace	·02
Carbonic dioxide	22·00	—
Silica	10·36	11·87
Phosphoric oxide	1·07	1·13
Sulphuric oxide	—	·90
Sulphur	·14	—
Water	4·45	—
	97·27	99·58

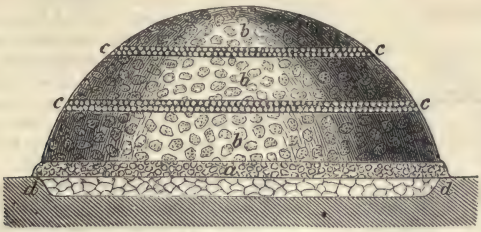
By reference to the foregoing analyses of different kinds of iron ore, it will be seen that in the case of the richer varieties of ore, calcination or roasting is seldom requisite as a preliminary operation for the purpose of separating volatilisable substances; but this treatment is nevertheless generally advantageous, inasmuch as it has the effect of disintegrating the ore and rendering it more susceptible of reduction in the smelting furnace.

The calcination of iron ore is carried out by heating it to dull redness in contact with air, either in heaps formed of alternate layers of ore and coal, or in kilns built of brick or stone, from which the roasted ore can be drawn out at the bottom. Careful regulation of the temperature to which the ore is heated is essential to the success of the operation, so as to ensure on the one hand the separation of all volatilisable substances and the proper disintegration of the ore without causing the formation of fusible silicates in the case of silicious ore, or the reduction of iron to the metallic state in the case of carbonaceous ore.

The method of calcination in heaps is cheapest as regards labour, and it offers full

opportunity for oxidation, but the consumption of fuel is large and the effect produced by the heat is irregular. Fig. 385 represents the construction of an ore heap consisting of alternate layers of ore (*bbb*) and of fuel (*acc*), the whole being placed on a bed of large lumps of ore (*dd*). Sometimes the ore heap is made rectangular and several feet long.

Fig. 385.

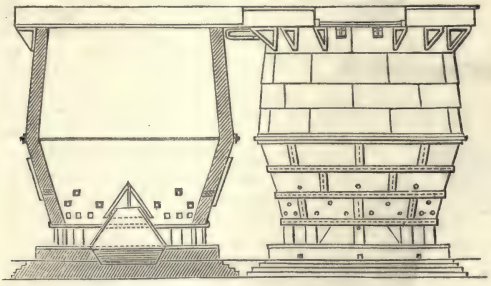


The Welsh method is to form in the open air a pile of about 5 ft. high having alternate layers of ore and coal, each coal layer being a few inches thick, and the ore layer about a foot in depth. When once lighted the pile burns so long as coal remains, and when the operation is properly carried on so as to prevent the ore fusing, there is a loss in weight of about 30 per cent. on the weight of ore taken. Black band ores of themselves contain sufficient carbonaceous material to continue the roasting when the pile has been ignited.

Roasting in kilns is, however, generally preferable to open-air roasting, on account of the saving in fuel and the more uniform condition of the residuary mass. The alternate layers of coal and ore are piled in a manner similar to open-air roasting. The kiln is kept charged by withdrawing the bottom layer of calcined ore, and running in a fresh charge at the throat.

The kilns used for the purpose are variously constructed, sometimes with a fire grate and sometimes without. Fig. 386 represents the circular kilns used at Middlesborough, which are made of cast-iron plates lined with fire brick, and supported upon hollow cast-iron pillars so that a space is left below for drawing out the calcined ore. Each kiln has a central cone of cast iron which spreads the ore outwards as it descends towards the openings from which it is drawn out. Round the lower part of the kiln are a number of holes for admitting air.

Fig. 386.



The consumption of fuel in roasting iron ore in these kilns amounts to about five per cent. of the weight of calcined ore.

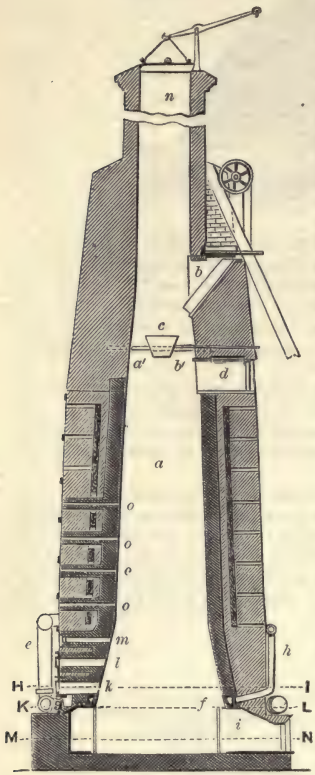
The height of these kilns is sometimes upwards of 30 feet, and the diameter 24 feet. A kiln having a capacity of 8,000 cubic feet is capable of calcining about 800 tons of ore per week.

The kilns used in Wales have a rectangular form; they are 18 feet high, 20 feet long, and are wider at the upper part than at the bottom: air is admitted on one side through apertures in the wall above the opening through which the roasted ore is drawn out. These kilns are built in ranges, with a tramway running along the top of them. The capacity of each kiln is such as to hold about 70 tons of ore, and the quantity of ore roasted amounts to about 146 tons per week.

The waste gas discharged from smelting furnaces is sometimes used as fuel for the calcination of iron ore, and the gas is burnt for this purpose in a kiln constructed in the manner represented in vertical and horizontal sections by figs. 387 and 387A.

The body of the kiln is in the form of a cylindrical shaft (*a*) from 6 to 10 feet diameter, at the upper end of which is a lateral opening (*b*) fitted with a sliding door, through which the iron ore is shot into the kiln, and when this is not being used the door is kept closed. As the iron ore falls into the kiln it is distributed by the hopper (*c*). The opening (*d*) admits of the examination of the kiln to ascertain whether it is sufficiently filled. At the bottom of the shaft (*n*) are several arched openings (*iii*, figs. 387 and 387A) through which the roasted ore is drawn out. The openings (*l m*) serve for inserting iron bars by which the mass of ore can be loosened, if requisite, when it is being drawn. The openings (*ooo*) at different heights serve as sight holes for regulating the temperature, and at the upper end of the shaft is a tall chimney (*n*) the mouth of which can be closed by a damper for regulating the operation. The combustible gas is led into the kiln from a pipe (*e*) passing round it, and enters through the channel (*g*) and the passages (*k*) in the brickwork, of which there are several, as shown in the horizontal section. The air requisite for combustion is supplied through the pipe (*h*) into a hollow ring extending round the kiln, and it escapes through several openings in this ring.

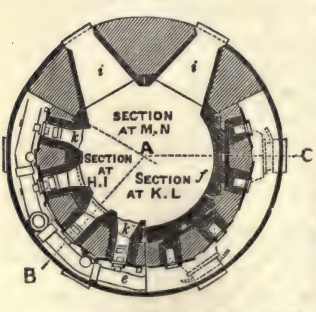
Fig. 387.



The chief disadvantage of this kiln is that the flame does not always penetrate to the centre of the mass of ore in the shaft, but passes up along the wall. This tendency can be counteracted by making the gas tube pass across the kiln under a strong cast-iron ridge extending from side to side, over which the roasted ore can slide down when it is drawn out.

Economy of fuel may in some cases be ensured by making the calcination of the ore the first stage in the series of changes that take place in the blast furnace, where the heat necessary for the purpose is obtained from the ascending current of gases. This process might probably be made more effectual by so increasing the height of the shaft that it might serve as a substitute for the calcining kiln, as in the Cleveland district, where blast furnaces 75 ft. high have been erected with this object; it is, however, doubtful whether the saving of fuel compensates for the disadvantages arising from the liability of some kinds of fuel and ore to be crushed by the weight of the column of materials in the shaft, and from the reduction in the calorific power of the discharged gases which can be advantageously used as fuel.

Fig. 387 A.



Formerly the coal used as fuel in smelting iron ore was always previously charred, so as to separate the volatilisable portion. This procedure involves a considerable waste of heating power, amounting to something like 39 per cent., but in some cases it is unavoidable, on account of the character of the coal employed. Thus, for instance, if highly bituminous caking coal were used in the raw state, there would be considerable risk of agglomerating the contents of the smelting furnace and disturbing the operation. With coal of a friable nature, there would be a danger of stopping up the furnace. However, when the coal is sufficiently hard, and does not cake when heated, it is now often used in the raw state.

In smelting iron ore for the production of pig iron, the reduction of the ferruginous oxide in the ore is effected chiefly, if not entirely, by means of carbonic oxide, the reaction in the case of ferric oxide being represented by the following equation :

$$\underset{160}{Fe_2O_3} + \underset{84}{3CO} = \underset{132}{3CO_2} + \underset{112}{2Fe}$$

according to which the iron thus produced amounts to rather more than three times the weight of the carbon consumed in the state of carbon oxide.

The supply of carbonic oxide requisite for this reduction is furnished by the combustion of the fuel used in the operation, and most likely the whole of the carbon it contains is burnt in such a manner as to yield only carbonic oxide in the first instance. The reaction by which ferric oxide is reduced may be regarded as the completion of the combustion of that portion of the fuel which takes part in it. Carbon in the state of carbonic oxide is in this way capable of reducing nearly four and a half times its weight of ferric oxide, and since the percentage amount of ferric oxide in iron ore generally ranges from 40 to 90 per cent., while the fuel used in smelting may be taken as containing on the average 90 per cent. of carbon, the fuel consumed in this part of the iron smelting process varies from about one-tenth the weight of the ore up to rather less than one-fourth in the case of very rich ores.

The conversion of the carbon supplied as solid fuel to the smelting furnace into a gaseous state by combination with oxygen is doubtless a circumstance of great importance as regards the reduction of the ferruginous oxide in the ore, for though ferric oxide is readily reduced when heated in contact with carbon, this condition would not be so easily attained in operating upon the large scale. By the formation of carbonic oxide however, and by the absorption of this gas by the porous lumps of ore, reduction is soon brought about by the reaction above referred to.

This reaction takes place at a temperature ranging between 140° and 400°, but most readily at a red heat. The extent to which it takes place when ferric oxide is heated with carbonic oxide is limited, and the complete reduction of ferric oxide cannot be effected by the proportion of carbonic oxide indicated in the above equation, since carbonic dioxide, which is one of the products of the reaction, is capable of giving up part of its oxygen to metallic iron when brought into contact with it at a temperature above 400°. Consequently the reduction of ferric oxide by carbonic oxide at a moderate red heat does not continue after the resulting carbonic dioxide has attained a proportion to the unaltered carbonic oxide of about one half its volume. To ensure complete reduction therefore the ferric oxide must be exposed to the action of a current of the reducing gas, so that the carbonic dioxide formed may be constantly swept away out of contact with the reduced iron.

Besides the reduction of the ferruginous oxide, it is essential to the production of pig iron that the reduced metal should combine with carbon and form a readily fusible carburet. The precise mode in which this takes place in smelting iron ore is not thoroughly understood, but it is highly probable that it is a result of the decomposition of carbonic oxide according to the following equation :

$$2CO = CO_2 + C.$$

Except in the case of very unusually rich iron ore, the reduction of the ferruginous oxides requires to be accompanied by the formation of a readily fusible compound of the earthy admixtures with which most kinds of iron ore are associated. These substances generally consist for the most part of silica, various silicates, clay, calcium carbonate, or some analogous minerals, as will be seen by reference to the tabulated analyses of the different varieties of iron ore, and as they are not only intimately mixed with the ferruginous oxide of the ore, but are also infusible at the temperature produced in iron smelting, their presence in such an infusible condition would offer a mechanical obstacle to the fusion of the reduced iron. In order to effect the separation of these admixtures, it is therefore necessary to convert them into readily fusible compounds. The double silicates containing two or more bases are substances whose fusibility and general characters correspond to the requirements of the case, and consequently in smelting iron the separation of the earthy admixtures in the ore is effected by the formation of a vitreous silicate capable of being readily melted so as to separate from the metal in the form of a slag.

The fusibility of the silicates varies considerably, not only according to the nature of the basic oxide they contain, but also according to the relative proportions of silica and basic oxide. Those containing only one basic oxide are moreover generally less fusible than the silicates containing two or more basic oxides, and the degree of fusibility is still further influenced by the relative proportion of the basic oxides, as will be seen from the following table of Plattner's results :—

Melting Points of Silicates.

Temperature of formation	Melting point	SiO_2	BaO	CaO	MgO	Al_2O_3	FeO	MnO	PbO	Ratio of oxygen in bases to oxygen in silica
2400°	—	64·3	—	—	—	35·7	—	—	—	1 : 2·0
2400°	—	73·0	—	—	—	27·0	—	—	—	1 : 3·2
2250°	—	59·8	—	—	—	—	—	—	—	1 : 2·0
2200°	—	69·0	—	—	40·2	—	—	—	—	1 : 2·8
2200°	—	29·1	70·9	—	31·0	—	—	—	—	1 : 2·1
2150°	—	52·0	—	48·0	—	—	—	—	—	1 : 2·0
2100°	—	61·8	—	38·2	—	—	—	—	—	1 : 3·0
2100°	—	37·6	62·4	—	—	—	—	—	—	1 : 3·0
2100°	—	48·6	10·0	41·4	—	—	—	—	—	1 : 2·0
2100°	—	45·0	20·0	35·0	—	—	—	—	—	1 : 2·0
2050°	—	54·0	20·0	—	—	26·0	—	—	—	1 : 2·0
2000°	—	55·5	—	25·8	18·7	—	—	—	—	1 : 2·0
1950°	—	57·5	—	26·5	16·0	—	—	—	—	1 : 2·0
1918°	—	40·5	—	37·2	—	22·3	—	—	—	1 : 1·0
1832°	—	47·0	—	—	—	—	53·0	—	—	1 : 2·0
1789°	—	30·5	—	—	—	—	69·5	—	—	1 : 1·0
Iron furnace slag										
—	1445°	58·0	—	22·0	10·0	6·0	2·0	2·0	—	1 : 2·2
1876°	1431°	50·0	—	30·0	—	17·0	3·0	—	—	1 : 1·5
Freiberg copper slags										
1730°	1360°	50·0	1·5	3·0	1·5	6·0	38·0	—	—	1 : 2·0
1690°	1331°	48·0	—	4·5	1·5	9·0	37·0	—	—	1 : 1·75
1546°	1345°	32·7	—	—	—	7·0	60·3	—	—	1 : 1·0
Freiberg lead slag										
1460°	1317°	36·5	—	4·0	3·0	8·5	40·5	—	7·5	1 : 1·25

The temperatures given as those at which the several silicates are formed and melted refer to the following melting points adopted by Plattner as standards of comparison:—

Platinum	2534°
Gold	1102°
Silver	1023°
Lead	334°

It seldom happens that the foreign substances associated with iron ore are of such a nature or present in such relative proportions as to produce under the influence of heat a silicate that would be suitable for the purposes of iron smelting. Hence it is necessary to mix with the ore some substance that will contribute to the formation of a fusible slag, by combining with the admixtures in the ore. The substance added with this object is termed flux, and its nature as well as the proportion in which it is used will of course depend upon the composition of the ore to be smelted.

When the ore contains calcareous substances a silicious material such as forge cinder or the roasted slag from the puddling furnace is added as a flux, or the ore may be mixed in suitable proportions with one containing silica or clay. In the more frequent case of ore containing silica, clay, or other silicates the material used as a flux is limestone or burnt lime, in order to effect the formation of a double silicate containing alumina and lime as its basic constituent.

The published analyses of iron slags are very numerous, and the general characters of them are indicated by the accompanying table.

The character generally considered to be indicative of the formation of a suitable slag consists in its being sufficiently liquid to separate perfectly from the metal, though as it flows from the surface it is generally somewhat viscous. When solidified the slag should not be vesicular, but compact and homogeneous, without being either very vitreous or stony. The colour of the slag from iron smelting furnaces varies very much, but it does not afford much indication of its character. When charcoal is used as fuel, the slag is lighter coloured than that from furnaces in which coke or coal is used.

Analyses of Slags from Blast Furnaces worked with Charcoal.

	Ullgren	Karsten						Rammelsberg
Ferrous oxide	0·95	1·45	0·2	—	2·44	21·5	0·06	1·27
Manganous oxide	1·86	1·40	11·6	4·30	2·20	29 2	33·96	3·16
Alumina	4·30	6·25	6·7	12·60	13·04	2·1	6·63	5·71
Lime	38·64	19·71	26·9	42·85	25·67	—	—	27·60
Magnesia	7·40	0·70	—	—	0·57	8·6	10·22	7·01
Potash	0·30	—	—	—	—	—	—	—
Soda	1·38	—	—	—	—	—	—	—
Silica	46·37	70·12	54·1	39·60	53·79	37·8	48·39	55·25
Phosphoric acid	trace	—	—	—	—	—	—	—
Sulphur	0·03	0·37	0·5	0·65	—	0·8	—	—
	101·23	100·00	100·00	100·00	97·71	100·0	99·26	100·00
Percentage of iron	0·740	1·130	0·160	—	1·900	16·72	—	0·990

	Hartz				Styria	Sweden		
	Rammelsberg			Bromeis	Wehrle	Oengren	Sjogren	Follin
Ferrous oxide	4·03	0·44	3·25	5·83	1·4	1·68	3·29	1·0
Manganous oxide	25·04	24·85	24·53	22·18	28·6	2·81	2·63	4·1
Alumina	5·88	4·96	11·27	5·12	2·6	6·62	5·38	5·1
Lime	20·56	26·66	21·55	20·00	10·4	19·35	19·81	18·0
Magnesia	2·41	1·10	0·82	2·18	1·3	10·46	7·12	13·3
Silica	39·99	41·49	38·58	43·58	54·6	58·60	61·06	58·1
Sulphur	—	—	—	1·11	1·1	—	—	—
	97·91	99·50	100·00	100·00	100·00	99·52	99·29	99·6
Percentage of iron	3·130	0·340	2·420	4·560	1·090	1·310	2·460	0·780

Analyses of Slags from Blast Furnaces worked with Coal.

	Dowlais			Dudley	Russell's Hall	Belgium	Russell's Hall	Cwm-Celyn
	Riley			Percy	Forbes	Percy	Dick	Noad
Ferrous oxide	3·08	6·91	0·76	1·27	0·93	4·94	1·00	19·80
Manganous oxide	1·02	1·67	1·62	0·40	2·79	2·26	2·20	1·53
Alumina	11·55	15·51	15·13	14·11	13·01	13·05	12·91	20·20
Lime	32·09	23·81	32·82	35 70	31·43	32·53	29·92	10·19
Magnesia	3·78	4·38	7·44	7·61	7·27	1·06	4·79	2·90
Potash	1·53	1·98	1 92	1·85	2·60	2·69	0·87	1·10
Silica	45·23	44·88	38·48	38·05	37·91	42·06	47·08	42·96
Phosphoric acid	—	0·43	0·15	—	—	0·19	0·05	—
Calcium	1·04	0·59	1·23	0·82	3 65	1·03	1·78	1·32
Sulphur	0·83	0·47	0·99					
	100·15	100·63	100·54	99·81	99·56	99·81	100·60	100·00
Percentage of iron	2·39	5·37	0·60	0·99	0·62	3·84	0·80	15·40

In smelting iron ore with charcoal the temperature of the furnace is generally lower than when coke or coal is used, and on that account the slag requires to be more fusible than in the latter case; on the other hand, when coke or coal is used as fuel the fusibility of the slag requires to be reduced by increasing the proportion of lime relatively

to silica and alumina to such an extent that the fusion of the slag may not take place until after the reduction of the iron has been completed. This is requisite in order to prevent the materials constituting the charge from becoming agglutinated, and to admit of their remaining porous while passing through that portion of the smelting furnace where reduction takes place. This is especially necessary when hot blast is used.

In smelting silicious iron ore there is a further necessity for the addition of lime, which is even more important than that relating to the production of a suitable fusible slag. This arises from the circumstance that the double silicate containing ferrous oxide and alumina is very fusible, and owing to the tendency to the formation of this silicate in smelting a silicious or argillaceous ore, the result would be that a considerable portion of the iron would escape reduction and be lost, besides the production of other serious inconveniences. The presence of a sufficient proportion of lime prevents the combination of ferrous oxide with the aluminous silicate in the ore, and in order to prevent it as much as possible the quantity of lime mixed with the ore is such as to form a silicate in which the oxygen of the basic oxides is equal to that of the silica. In some kinds of iron ore the relation existing between the silica and alumina is very different from that generally obtaining in the clay iron ore of the coal-measures, as will be seen from the following table and by reference to the analyses of ores:—

	Low Moor	Brierley	Stanton	Butterley	Parkgate	Cleveland
Alumina . . .	23	24	20	26	24	25
Lime	9	9	13	11	13	27
Magnesia . . .	8	7	17	9	19	14
Silica	60	60	50	54	44	34
	100	100	100	100	100	100

In consequence of this difference, and the greater proportion of alumina in the ores of the Cleveland district, the slags produced in smelting them are much more stony and less vitreous than those produced in smelting other kinds of ore. The relative deficiency of silica as compared with alumina probably renders the slag much less fusible, and may serve to account for the apparent necessity for a very high temperature in smelting the Cleveland ore.

Analyses of Slags from Cleveland Ores.

	Crowder	Clarence Laboratory			
Ferric oxide . .	—	—	—	—	8·20
Ferrous oxide . .	0·72	3·64	0·61	0·32	—
Manganous oxide .	0·35	1·02	trace	0·80	—
Zinc oxide . .	—	—	—	—	4·60
Alumina . . .	24·69	20·72	22·28	21·70	16·00
Lime . . .	40·00	36·88	40·45	38·72	12·15
Magnesia . . .	3·55	4·25	7·21	6·10	0·57
Potash . . .	0·46	0·50	—	—	0·40
Soda . . .	0·99	—	—	—	6·85
Silica . . .	27·65	30·40	27·80	29·92	34·82
Phosphorus . .	0·26	—	—	0·07	—
Sulphur . . .	1·95	1·34	2·00	1·61	8·80
Chlorine . . .	—	—	—	—	1·56
Water . . .	—	—	—	—	5·60
	100·62	98·75	100·35	99·24	99·55
Percentage of iron .	0·560	2·830	0·470	0·250	—

As already mentioned, the conditions under which fuel is burnt in smelting iron ore for the production of pig iron are such that greater part of the carbon is converted into carbonic oxide, and with the exception of those portions which are converted into carbonic dioxide in the reduction of ferric oxide and the carburation of the reduced iron, the whole of the carbonic oxide is discharged from the smelting furnace, together

with the nitrogen of the air consumed in supporting combustion, the carbonic dioxide separated from the limestone used as flux, and the hydrogen or hydrocarbon vapour derived from the fuel. The following table gives the percentage composition by volume of the gas discharged from iron smelting furnaces in several different localities :—

Composition of Furnace Gas.

	Cleveland	Veckerhagen	Bärum	Audincourt	Clerval	Seraing	Alfreton
	Bell	Bunsen	Langberg and Scheerer	Ebelmen			Bunsen and Playfair
Carbonic oxide .	26·7	24·20	8·04	25·24	24·65	28·93	25·97
Carbonic dioxide	11·7	8·77	22·20	12·59	12·01	11·39	7·77
Nitrogen . .	60·9	62·34	64·43	55·62	57·22	56·64	55·35
Marsh gas .	—	3·36	3·87	—	·93	—	3·75
Olefiant gas .	—	—	—	—	—	—	·43
Hydrogen. .	·7	1·33	1·46	6·55	5·19	3·04	6·73
	100·0	100·00	100·00	100·00	100·00	100·00	100·00

Since the gas contains almost the whole of the carbon in the fuel consumed, and it is chiefly in the state of carbonic oxide, the gas is combustible, and admits of being usefully employed as fuel for various purposes connected with the smelting operation, so as to effect a considerable economy of fuel.

Pig iron or cast iron.—There are two distinctly different kinds of carburetted iron; one in which the carbon is entirely combined with the iron, and another in which the greater part of the carbon is not in a state of combination, but is disseminated throughout the mass in the form of minute crystalline laminæ.

White cast iron varies in colour from tin white to pale grey. It is very hard and brittle, has a crystalline lamellar texture, and is sometimes vesicular. The fracture is bright, and it varies from lamellar to compact and conchoidal, in proportion as the colour is tin-white or grey. The most characteristic variety is called specular iron. The amount of carbon varies from 3·5 to 5·24 or 5·75 per cent.

Grey cast iron varies in colour from pale grey to dark grey. It has generally some slight degree of malleability, but is much harder and more brittle than malleable iron. Its texture is granular, sometimes very fine grained, sometimes coarse grained at the fracture, with minute particles of graphite visible throughout the mass. The amount of carbon varies from 2 to 4·65 per cent.

The specific gravity of white cast iron is on the average 7·5, that of grey cast iron is about 7·1.

Grey cast iron melts at about 1600°, and more easily in proportion as the amount of carbon is greater. White cast iron melts at a lower temperature, but it does not become so liquid when melted as grey cast iron, which passes suddenly from the solid to the liquid state, while white cast iron remains for some time in a pasty condition. White cast iron when cooled very gradually from the melted state is converted into grey cast iron. On the contrary, grey cast iron, when slowly cooled from the melted state, is not altered, except in becoming softer and more malleable; but when cooled rapidly, it is converted into white cast iron more completely in proportion as the amount of carbon it contains is large. On this account the outer surface of a casting has a hard crust or skin in consequence of the more rapid cooling and solidification of that portion of the melted metal which comes into contact with the sides of the mould, and its conversion into white cast iron. This effect is often augmented in practice by lining the mould with iron plates so as to faciliate the solidification of the outer portions of the casting, and form a layer of white cast iron from $\frac{1}{8}$ to $\frac{1}{4}$ of an inch thick, while the interior retains the condition of grey cast iron, thus combining the particular advantages of white cast iron as regards hardness and of grey cast iron as regards strength. Melted cast iron dissolves malleable iron and is thus rendered tougher and stronger.

It has been observed that in large masses of cast iron there is an inequality in the amount of carbon contained in the metal at the exterior and interior portions. There is also a further difference as to the condition in which the carbon exists. At the centre the relative proportion of graphitic carbon as compared with combined carbon is greater than it is at the exterior portions. This difference is more marked

in proportion as the melted metal is more rapidly solidified at the surface. In one instance referred to by Karsten the following relations obtained :—

	Total Carbon	Combined Carbon	Graphite
Cast iron before melting	4·0281	·7812	3·2469
Outer white portion of casting	5·0929	5·0929	
Inner grey portion of casting	3·8047	·6106	3·1941

Between the two extremes of white and grey cast iron there are a number of intermediate states in which the white and grey varieties are mixed together in different proportions, constituting what is termed mottled cast iron. The hardness and strength of these varieties of cast iron differ considerably; as a rule, the grey iron is stronger than white iron, while this is harder than the grey. White cast iron is however too brittle to be used for structural purposes, except for the purpose of coating the surface of castings with a hard skin or crust by chill casting, as already described.

The tenacity of cast iron is very much less than that of malleable iron, but its capability of resisting crushing force is very much greater.

	Direct tenacity	Resistance to direct crushing	Modulus of rupture of square bars	Modulus of elasticity
	In pounds per square inch			
Cold blast cast iron .	from 12,694 to 18,855	56,455 102,408	36,693 39,609	14,000,000 17,036,000
Hot blast cast iron .	from 13,434 to 23,468	72,193 104,881	29,889 43,497	11,539,000 22,733,000
Toughened cast iron .	from 23,461 to 25,764	129,876 119,457	— —	— —

The strength of cast iron is increased by remelting, but reduced when the melting is repeated several times. At very low temperatures it becomes more brittle and weaker.

The specific heat of specular iron is 0·12983, that of ordinary white cast iron is 0·12728.

The linear expansion of cast iron is greater than that of malleable iron, amounting to $\frac{7}{560}$ between 20° and 560° (red heat) and $\frac{12}{560}$ between 20° and a white heat.

Pieces of cold cast iron thrown into the melted metal sink to the bottom, but when they have a temperature near the melting point they float on the surface of the melted metal. Hence it would appear that some contraction takes place in the passage from the solid to the liquid state. This character is important as regards the application of cast iron to casting, for the increment of bulk attending solidification ensures the perfect filling of the moulds at that moment, and the production of sharp, well-defined castings. But the greatest amount of expansion or contraction takes place just below the melting point. On account of this contraction between a temperature near the melting point and the ordinary atmospheric temperature, it is necessary to make the mould for castings proportionately larger than the castings are required to be. The contraction for grey cast iron amounts to about one per cent., that of white cast iron is from 2 to 2·5 per cent. of the linear dimensions. The allowance generally made for this shrinkage in casting is $\frac{1}{96}$ or one-eighth of an inch to the foot. Cast iron also undergoes a permanent increase of bulk under the long continued influence of heat.

White cast iron exposed to an oxidising atmosphere at the ordinary temperature rusts much more slowly than grey cast iron, and this again, provided it does not contain much sulphur or other readily oxidisable substances, rusts more slowly than malleable iron. Specular iron is but very little liable to oxidation under ordinary atmospheric conditions.

At an elevated temperature grey cast iron becomes coloured by oxidation sooner than malleable iron; white cast iron, on the contrary, becomes coloured even sooner than steel. When cast iron is heated to redness in contact with atmospheric air, the carbon it contains is first oxidised and the metal is rendered somewhat malleable; then a crust of ferroso-ferric oxide is formed at the surface, which gradually increases in thickness.

Grey cast iron is most slowly oxidised in this way, and after the removal of its carbon it becomes porous and friable. White cast iron is decarburised more rapidly, and it acquires a malleable steely character. Upon this fact is based the manufacture

of malleable cast iron, which consists in heating to redness small castings imbedded in powdered charcoal, chalk, or ferric oxide, so as to be partially protected from the oxidising influence of the air.

Cast iron melted in contact with atmospheric air becomes covered with a crust of oxide, and by continually removing this crust as it is formed, the whole mass may be converted into oxide; if the crust of oxide be allowed to remain in contact with the melted metal, this gradually becomes decarburised, steely, and less readily fusible. White cast iron heated in contact with atmospheric air till it assumes a pasty condition is decarburised much more rapidly than by mere heating to redness, and it passes from the steely condition to that of pure iron, without so great a degree of oxidation as takes place when the metal is melted. The most important method of manufacturing malleable iron is based upon this fact.

Cast iron melted under alkaline or earthy carbonates is gradually decarburised and may be wholly converted into malleable iron, if the heat be sufficiently raised, as the iron becomes less fusible.

Atmospheric air forced into melted cast iron oxidises the carbon and silicon, as well as part of the iron, and converts the remainder into malleable iron. The temperature produced in this way is sufficiently high to determine the fusion of the wholly decarburised iron.

White cast iron heated with concentrated hydrochloric acid is entirely dissolved; but grey cast iron heated in the same way leaves a residuum of graphite. In both cases the combined carbon of the cast iron enters into combination with a portion of the nascent hydrogen eliminated by the solution of the iron, forming volatile oily hydrocarbons, the vapour of which communicates a peculiar smell to the gas evolved. The oily substance, which appears to be of a nature analogous to petroleum, also collects as a thin film on the surface of the liquid.

The action of dilute hydrochloric acid upon cast iron is somewhat different. Specular iron is acted upon very slowly at the ordinary temperature; but, with the aid of heat, both it and grey cast iron are readily dissolved. The hydrogen gas evolved has the characteristic smell, but the amount of hydrocarbon formed appears to be less than when concentrated acid is employed. White cast iron leaves a bulky dark brown carbonaceous residue which is soluble in potash, and when washed and dried is very readily combustible, leaving a black residue containing silica. Grey cast iron leaves a residue consisting partly of graphite, partly of a carbonaceous substance similar to that obtained from white cast iron, and partly of another black carbonaceous substance that is magnetic, taking fire on contact with the air, and leaving a residue of ferric oxide when burnt.

Cast iron is slowly acted upon by sea water. Cannon balls that had been lying in the sea off the coast of Normandy since 1692 were found to have lost two-thirds of their original weight, and had been converted into a substance that could be cut with a knife, the metallic iron having entirely disappeared. Cannon balls taken from vessels that had been sunk fifty years before near Carlscrona were found to be partly converted into a grey porous graphitic substance, which after exposure to the air for a quarter of an hour in a moist condition became so heated that the adherent water was converted into steam. The substance remaining after the action of sea water upon cast iron appears to be very similar to that remaining, mixed with graphite and the bulky carboniferous substance, after dissolving grey carbon by dilute hydrochloric acid. Karsten considered it to be a compound of iron with three atomic proportions of carbon. Berzelius ascribed the solution of cast iron by sea water to the conjoint action of carbonic acid and oxygen; wherever cast iron is exposed to the combined influence of fresh water and sea water by tides, this solvent action takes place more rapidly than in sea water.

Cast iron generally contains besides iron and carbon some other substances, especially manganese, silicon, phosphorus, sulphur, arsenic, copper, etc., the amounts varying considerably, as shown in the accompanying analyses (see p. 568), and some of these substances appear to exercise considerable influence in modifying the characters of the metal.

Silicon is almost always present in pig iron to some extent. It originates from the deoxidation of silica in the process of smelting and the amount varies very much. In white cast iron it generally ranges from 0·1 to 0·5 per cent.; in grey cast iron the amount is larger, being seldom less than 0·5, and sometimes exceeding 3 per cent. Karsten found 3·45 to be the maximum amount of silicon in pig iron. The greater amount of silicon in grey cast iron is considered to be due to the circumstance that it is produced at a higher temperature than white pig iron. Iron produced with hot blast also contains more silicon than that smelted with cold blast.

It is generally considered that within the ordinary limits of from 0·5 to 3 per cent. the presence of silicon in cast iron does not exercise any prejudicial influence upon the

quality of the metal; but since it is very detrimental to malleable iron, and reduces its tenacity, it is essential that in the conversion of cast iron into malleable iron the silicon should be separated as much as possible. The greater the amount of silicon in pig iron, the greater also is the waste of metal incurred in its conversion into malleable iron by the puddling operation.

Locality. Kind of pig	Fe	Mn	C		Si	S	P	Analyst
			Combined	Graphitic				
Styria (specular iron)	94·68	·98	3·88	—	·41	·02	·04	Widtermann
Müsen „	82·86	10·707	4·323	—	·997	·014	·059	Fresenius
Bohemia „	—	22·183	2·311	—	2·732	—	—	Richter
Damemora „	92·906	1·987	4·809	—	·176	trace	·122	Henry
„ „	95·57	·10	4·2	—	·08	„	·05	„
New Jersey „	81·363	11·50	6·9	—	·10	·137	—	„
Tow Law „	—	2·37	4·1	—	·23	·03	·073	Tookey
Clyde (white pig iron)	92·24	2·60	·3	1·52	1·79	·60	·95	Berthier
Dowlais	95·10	·14	2·84		1·21	·46	·64	Riley
Blaenavon (forge pig)	—	·22	2·37		1·09	·73	·76	W. A.
Whitehaven (No. 4)	—	·07	·35	1·86	2·63	·10	·03	Berthier
Russell's Hall (No. 4)	92·82	·72	·19	2·45	2·07	·32	1·43	Henry
Clyde (foundry)	94·63	·50	1·20	1·40	1·53	·35	·39	Berthier
„ „	92·30	—	·40	1·80	2·80	1·40	1·30	„
Dowlais (No. 3)	94·36	·50	·04	3·10	2·16	·11	·63	Riley
Park End (No. 1)	—	·23	—	3·26	2·34	·04	·14	W. A.
„ (grey forge)	—	·14	—	3·08	2·18	·06	·14	„
Pontypool (grey pig)	—	·42	—	2·53	1·23	·08	·46	„
Blaenavon (No. 3)	—	·66	—	2·64	1·68	·08	·27	„
„ (No. 1)	—	·28	—	3·40	1·36	·07	·29	„
Tow Law (No. 1)	90·584	1·837	—	2·795	4·414	·039	·099	Riley
Weardale (No. 1)	—	1·45	—	3·24	1·80	·04	·19	W. A.
„ (No. 2)	—	1·04	—	2·26	4·25	·06	·07	„
„ (No. 3)	—	trace	—	2·15	1·18	·12	·19	„
Stockton-on-Tees (No. 3)	—	·06	—	3·31	1·43	·03	1·36	„
South Bank (No. 2)	—	·38	—	3·04	2·73	·04	1·30	„
Whitehaven (No. 1)	—	·11	—	3·22	3·02	—	·06	„
„ (No. 2)	—	·07	—	2·24	2·77	·01	·05	„
Newland	—	—	—	2·83	·59	·03	·10	„
Beeston (No. 3)	—	1·00	—	2·83	2·17	·05	·55	„
„ (No. 4)	—	·61	—	2·76	1·80	·84	·55	„
Bowling (No. 1)	—	—	—	2·90	1·94	·04	·57	„
„ (No. 3)	—	—	—	2·80	1·51	·06	·44	„
Butterley (No. 2)	—	1·06	—	2·74	2·36	·02	1·21	„
„ (No. 4)	—	·40	—	2·60	1·34	·11	·75	„
West Hallam (forge pig)	—	·94	—	2·57	1·53	·05	·70	„
„ (foundry	—	·60	—	2·40	1·50	·06	·34	„
Wellingbro' (No. 1 grey)	—	·24	—	2·85	1·92	·10	1 19	„
„ (mottled)	—	·08	—	2·10	2·11	·13	1·07	„
Goldendale	—	·98	—	2·54	2·71	·04	1·07	„
Netherton (forge pig)	—	·13	—	2·81	·57	·06	·29	„
Dudley (grey pig)	—	·49	—	2·61	1·40	·04	·72	„
„ „	—	·06	—	2·56	1·75	·05	·63	„
„ „	—	—	—	3·21	1·54	·07	·23	„
„ „	—	—	—	3·34	1·18	·07	·55	„
„ „	—	—	—	2·87	1·16	·08	—	„
India „	—	·14	—	3·38	·44	·04	·27	„
Nova Scotia (No. 1 grey)	94·85	·44	—	3 50	·84	·02	·19	Tookey

Sulphur is almost always present in cast iron, but sometimes the amount is so very small that it can scarcely be determined. In good cast iron the sulphur probably never reaches 0·5 per cent. Pig iron smelted with mineral fuel always contains more sulphur than that smelted with charcoal, in consequence of the sulphur present in the coal or coke being transferred to the iron. The presence of sulphur in cast iron renders the metal more fusible, but also more liable to solidify sooner when slightly cooled below the melting point, so as to become quite viscid while still red hot. When specular iron is melted with sulphur, carbon is separated, and it collects

upon the surface of the melted metal in the form of graphite, which differs from ordinary graphite in having no lustre. Grey cast iron melted with sulphur is converted into white cast iron, containing a larger amount of carbon than the original grey iron, as shown by the following results obtained by Karsten:—

	The grey cast iron contained in 100 parts.	The resulting white iron contained in 100 parts.
Combined carbon	0·6253	5·4878
Graphite	3·3119	—
Sulphur	0·0286	0·4464

Hence it appears that while sulphur displaces carbon existing in combination, still up to a certain point the carbon so displaced from combination with one portion of iron is taken up by another portion, until no more can be taken up. The presence of sulphur in cast iron appears, therefore, to determine the existence of the carbon in a state of combination with the iron, and thus to conduce to the production of white cast iron.

Phosphorus is frequently present in cast iron, sometimes to the extent of one or two per cent. When amounting to more than 0·5 per cent., it renders the metal brittle but more fusible, very liquid when melted, and capable of remaining much longer in the liquid state. Within certain limits, therefore, the presence of phosphorus in iron intended for casting is advantageous rather than otherwise.

Manganese is frequently present in cast iron, and it appears to have some influence in determining a high degree of carburation of the iron, as well as the existence of the carbon in a state of combination with the iron, so that its presence in the materials used in smelting tends to bring about the production of white cast iron.

Nitrogen is frequently present in very small proportion in pig iron, and it appears to have a considerable influence on the character of the metal. Schafhäutl estimated the amount of nitrogen in several kinds of cast iron as follows:—

White cast iron	0·764 per cent.
Grey cast iron	0·720 „
Specular iron	1·200 „

Marchand's experiments led him to doubt the existence of nitrogen in cast iron, and to infer that, if it were present, it never amounted to 0·02 per cent. Bouis, on the contrary, considered that nitrogen is often present in cast iron, and he has stated that very hard cast iron containing much manganese will contain 0·15 per cent. of nitrogen.

Arsenic. There is much difference of opinion as to the influence of arsenic upon iron, and as to the frequency of its presence; but there are some well-established instances of cast iron containing a considerable amount of arsenic. Wöhler found it in four samples of pig iron, and Schafhäutl has stated that the pig iron made at Alais from an arsenical ore contained from 2·5 to 4 per cent. of arsenic. According to Berthier's analyses of some iron shells and shot from Algiers, the metal contained from 9·8 to 27 per cent. of arsenic, constituting a true alloy; and more recently a wrought-iron shot from Sinope has been found by Wood to contain 16·2 per cent. of arsenic. Karsten however never detected arsenic in pig iron.

The presence of small amounts of arsenic in cast iron is considered to have the effect, like phosphorus, of rendering the metal more fusible, brittle, and weaker.

Titanium appears to be frequently present in some kinds of cast iron, and it has been supposed to improve the quality of the metal. The following analyses of titaniferous pig iron by Riley show the extent to which it is present:—

Iron	93·47	92·79	92·04	87·90	86·88	84·26
Carbon	—	—	—	·31	1·02	·07
	3·31	3·18	3·11	3·12	3·01	2·61
Silicon	1·86	3·28	3·55	2·59	2·55	3·32
Titanium	1·15	·71	·47	·79	1·15	1·63
Sulphur	·06	·06	·11	·03	·03	·02
Phosphorus	·08	·06	·09	·15	·15	·20
Manganese	·05	·48	1·09	5·85	6·37	8·09
Nickel and cobalt	—	—	—	·06	0·11	—
Copper and antimony	—	—	—	·06	·04	·06
	100·437	100·56	106·46	100·85	100·31	100·27

Vanadium has also been found in the pig iron made from the ores of Taberg in Sweden, and in pig iron made from the Seend ore of Wiltshire.

Chromium has been found in some kinds of pig iron, but there is no evidence to show whether it has any influence on the character of the metal.

Copper is not unfrequently present in pig iron. When exceeding 0·2 per cent., it is said to render the metal harder, tougher, and stronger.

Zinc is sometimes present in pig iron smelted from ores containing zinc, and Karsten found cast iron containing traces of zinc to be very soft, but rotten and brittle.

Aluminum, magnesium, calcium, and potassium are sometimes indicated by analyses as existing in very minute proportion in some kinds of pig iron, but scarcely anything is known of their influence on the characters of the metal.

The furnace used in the smelting of iron ores consists of a cylindrical chamber, the lower portion of which forms a hearth where the melting of the reduced ore and flux takes place, while the upper portion of the chamber, termed the shaft, serves as a receptacle for the charge while it is undergoing the chemical changes produced by the heated gases resulting from the combustion of the fuel. This takes place at the lower part or hearth of the furnace, and is promoted by a powerful blast of air, the term blast furnace being on that account generally applied to iron-smelting furnaces. According to the kind of fuel used, the nature of the ore to be smelted,

Fig. 389.

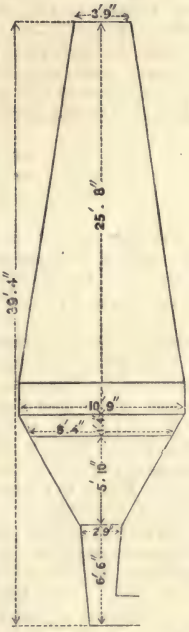


Fig. 388.

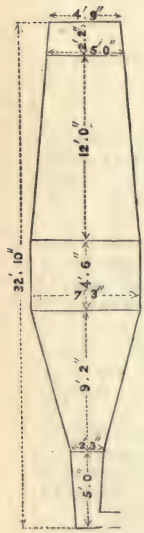
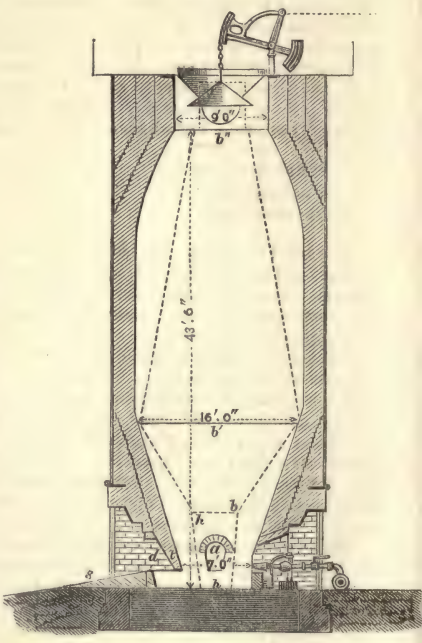


Fig. 390.



and a number of other circumstances, the form and dimensions of the blast furnace vary considerably, as shown by the accompanying sections of the Norwegian charcoal furnace (fig. 388), and the blast furnace formerly used in this country (fig. 389).

One of the most approved modern forms of blast furnace is represented in vertical section by fig. 390. The shaft is cylindrical, and is gradually contracted towards the hearth, differing considerably in this respect from the older form of smelting furnace, the interior sectional contour of which is represented by the dotted outline shown in the figure, the shaft (b' b'') having a conical form, the hearth being much more contracted, while the side of the furnace between the upper part of the hearth at b and the lower extremity of the shaft at b' is considerably inclined, forming a decided angle at its junction with the shaft and with the hearth.

At one side of the hearth (h) there is an opening formed by an arch (t), called the tymp, and below this arch the hearth is prolonged some distance beyond the plane of

the tymp, as far as the block of stone (*d*) called the dam, which serves to retain the melted iron in the hearth, while the melted clay, floating on the surface of the iron, flows away through a depression in the upper surface of the dam called the cinder notch, along an inclined plane called the cinder fall (*s*). Through the bottom of one side of the dam there is a channel called the tapping hole, communicating with the hearth, to admit of the melted metal accumulating in the hearth being run out at intervals. This channel is stopped up with sand or clay while the smelting operation is going on, and until the hearth is filled with metal. The side of the furnace at which the dam is situated is called the front, and the opposite side is called the back. At the side of the furnace there is an arched opening called the tuyere hole, and in many instances there are similar openings at the other two sides.

Air is supplied to the furnace through pipes connected with a powerful blowing engine, and furnished with conical tubes called tuyeres, extending into the furnace as far as the inner surface of the hearth wall. Each tuyere is surrounded with a hollow conical sheath, through which a stream of water is passed to prevent the tuyere from melting. In many cases the air supplied to the furnace in smelting iron ore is previously heated by making it pass through a series of cast-iron pipes which are heated externally. By this means the air is sent into the smelting furnace with a

FIG. 391.

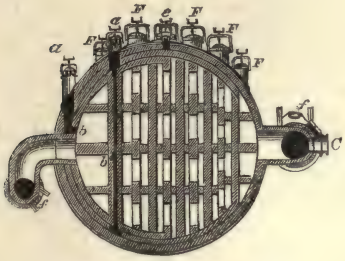


FIG. 392.

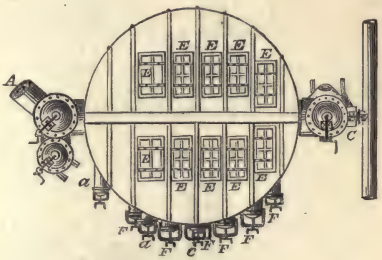


FIG. 393.

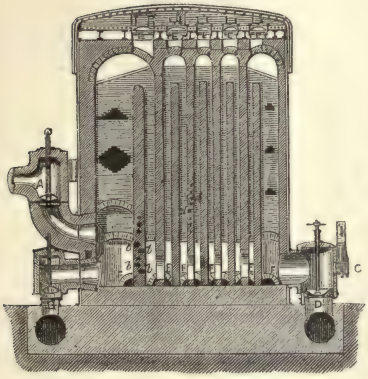
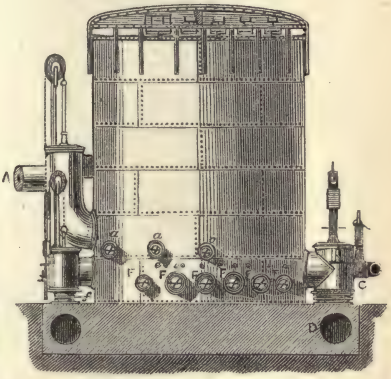


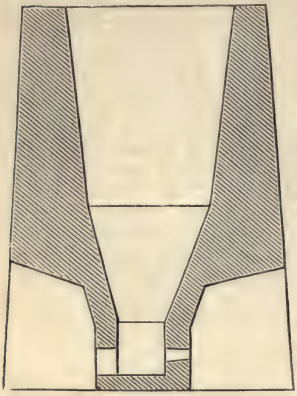
FIG. 394.



temperature varying from 100° to 400°, or even 700°. Within the last few years, great improvements have been made in the arrangements for heating the blast by the regenerative system introduced by Siemens. One of the stoves used for this purpose is represented by figs. 391 to 394. It consists of a series of parallel walls of fire-brick enclosed in a brickwork chamber, the spaces between the walls being separated by partitions, so as to form a number of rectangular channels, which are alternately heated by the combustion of the gas discharged from the top of the smelting furnace, and cooled by passing through them the air supplied to the furnace. The gas from the furnace is admitted through the valve (*f*) and, after being burnt in the oven, it escapes through the valve (C) to the chimney. After the mass of brickwork has been sufficiently heated, cold air is admitted through the valve (D) and passes through the oven, escaping from the valve (A) to the smelting furnace. The doors (E, F) at the

top and bottom of the oven are for cleaning out the dust which accumulates in the brickwork channels. The apertures (a, b) are to admit air for the combustion of the gas.

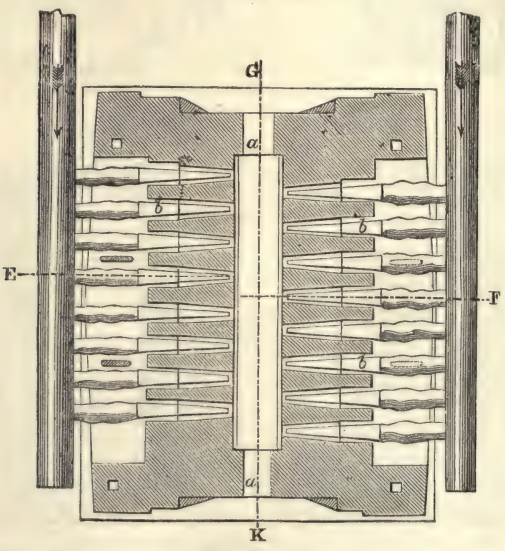
Fig. 395.



Of late years the capacity of iron smelting furnaces has been very considerably increased, and in some localities furnaces of 30,000 or 40,000 cubic feet capacity, and from 80 to 100 feet high, have been constructed. The chief alteration of shape has consisted in approximation to the cylindrical shaft, but it has been proposed to facilitate the uniform descent of the charge by using a furnace with an enlarged mouth, as shown by fig. 395. With the object of ensuring uniform distribution of the blast and equal temperature in the hearth, a furnace of similar section, but with a long narrow hearth, has been introduced by Rachette. The general arrangement of this furnace is represented by figs. 396 and 397. On each side of the hearth ($a\,a$), are a number of tuyeres ($b\,b$).

In working the blast furnace the shaft is kept nearly full, the iron ore, flux, and fuel constituting the charge being shot in at intervals through the throat, as the contents of the shaft sink down. Meanwhile, a continuous supply of air is forced into the lower end of the furnace through the tuyeres, under a pressure of from half a pound to two pounds per square inch in charcoal furnaces, and from two pounds to five pounds per square inch in furnaces worked with coal or coke. The supply of air must be proportionate to the size of the furnace and

Fig. 396.



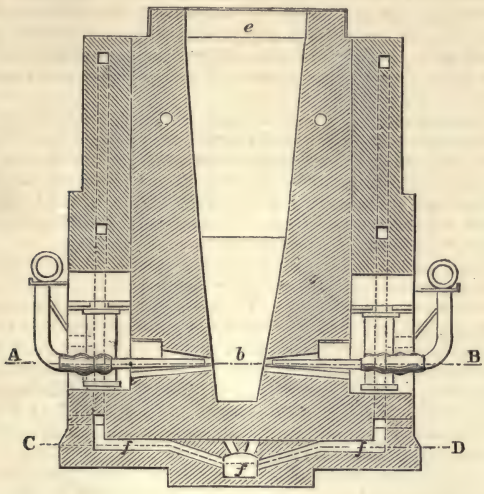
its rate of working, so as to maintain a rapid combustion of the fuel at that part of the furnace immediately above the level of the tuyeres.

The upper extremity of the furnace shaft is generally contracted, so as to form an aperture nearly one half the diameter of the shaft, which is termed the throat, and it is generally surrounded by a low wall or chimney called the tunnel head, having arched openings at the side for introducing the materials of the charge into the furnace. Iron smelting furnaces are sometimes worked with the throat open, but sometimes the gaseous products given off are collected; the throat of the furnace is then fitted with a hopper, which can be closed by a movable cone as shown in fig. 390, and the gas is led away through a tube to the furnace, where it is used as fuel.

In consequence of the different physical conditions of the several products result-

ing from the changes that take place in the materials used in smelting iron ore, those products are continuously discharged from the smelting furnace in a manner exactly the reverse of that in which the raw materials are supplied, the melted iron and slag flowing out at the bottom, while the gaseous products of combustion escape from the throat of the furnace.

Fig. 397.



The kind of fuel employed in smelting iron ore has a great influence upon the mode of working. With porous bulky fuel such as charcoal, combustion takes place more readily than when the more compact and denser kinds of mineral fuel are used, and, owing to the greater liability of charcoal to crumble under pressure, the furnaces in which it is used are generally much smaller than those worked with coal or coke. Owing to the relatively small amount of earthy substances in charcoal, and its entire freedom from sulphur and phosphorus, the iron melted with charcoal is always much purer than that smelted with mineral fuel, which is often prejudicial to the quality of iron.

Though the weight of the solid materials constituting the charge amounts to from four to five tons per ton of pig iron made, according to the kind of ore, flux, and fuel used, or even to seven tons and upwards when the materials are used in the raw state, by far the greater quantity of the total material supplied to a blast furnace in smelting iron consists of the atmospheric air by which combustion is supported. Taking carbonic oxide to be the ultimate product, the quantity of air needed to supply sufficient oxygen for combustion would amount to at least five times the weight of the fuel burnt. Consequently the total quantity of air supplied to a blast-furnace per ton of pig iron made according to the consumption of fuel will be as follows:

	Tons	Cwt.	Tons	Tons
Fuel consumed	1	3	2	3
Quantity of air	5	15	10	15

The greater part of the oxygen in this air is consumed in burning that portion of the fuel exclusively concerned in the production of a temperature high enough for effecting fusion of the slag and the reduced iron, and that part of the oxygen which is consumed in producing the carbonic oxide requisite for the reduction of the ore does not amount to quite half the weight of the iron obtained.

The temperature of the gas produced by the combustion of the fuel in smelting iron ore, and discharged from the throat of a blast-furnace, differs according to the kind of materials used in the smelting operation, the height of the furnace shaft, and the mode of working. In the case of charcoal furnaces, the escaping gas has generally a temperature ranging from 300° to 400°, while that from furnaces worked with coal or

coke is much hotter, usually ranging from 500° to 600° and upwards, according to circumstances. The whole of the heat corresponding to the temperature of the discharged gas is waste heat, except in so far as it has served at an earlier stage of the operation to produce the high temperature requisite for the fusion of the reduced metal and slag at the lower part of the furnace; and it is only by applying that heat to other purposes for which it may be available that it is possible to realise the full economical efficiency of the fuel consumed in the smelting of iron ore.

The extent to which the heat generated in smelting iron ore is thus dissipated, without producing the full useful effect of which it is capable, may be judged of from the fact that the weight of the gas discharged from a blast furnace exceeds the joint weight of the air and fuel consumed, amounting to from eight to seventeen times the weight of the pig iron produced.

But besides the waste of heat due to the high temperature of the discharged gas, there is a further and even more considerable waste of heat resulting from the circumstance that the product of combustion is carbonic oxide. Consequently the gas discharged from the furnace contains a very large proportion of carbonic oxide, together with some hydrocarbon vapour and hydrogen, and in all ordinary cases, at the temperature at which it escapes from the furnace, it is sufficiently inflammable to take fire on coming in contact with atmospheric air.

The consumption of fuel in iron smelting is one of the most important points connected with the economical production of this metal, and it is exceedingly desirable to reduce it to the lowest possible limit. The amount of fuel consumed per ton of pig iron made varies considerably, not only according to the kind of fuel, its calorific power, combustibility, texture, &c., but also according to the kind of ore operated upon and numerous other circumstances. Among these the shape of the furnace has an influence, in so far as it admits of the easy and uniform descent of the charge in the shaft. Another most important difference in the consumption of fuel is that resulting from the use of air at the ordinary atmospheric temperature, or air previously heated to a temperature considerably higher.

So great is the influence exercised by the use of heated air, that in charcoal furnaces the consumption per ton of pig iron made varies from half a ton to two tons and upwards, according as hot or cold air is used. In smelting with coal or coke the consumption usually amounts to from two to three tons and upwards with cold blast, and with hot blast it is from 23 cwt. to two tons.

This economy in the consumption of fuel is to a great extent effected by utilising as fuel the combustible gas which is discharged from the throat of the smelting furnace, and thus turning to account the heat that would otherwise be wasted. Sometimes also the air-blast is heated by fuel of a cheaper kind than that used in the smelting furnace.

In either case, since the temperature of the air is raised to from 327° to 700° and upwards, a considerable quantity of heat is thus conveyed into the smelting furnace, and proportionately less fuel requires to be burnt in the furnace. Moreover the carbon of the fuel burnt in the smelting furnace is for the most part only converted into carbonic oxide, while in the case of the fuel burnt in heating the blast it is converted into carbonic dioxide, and thus produces more than three times as much heat as when burnt in the smelting furnace. The full advantage of this difference in heat production is not indeed realised in the smelting furnace, since a portion of the heat developed is carried off in the product of combustion from the hot air stoves, and a further portion is lost by radiation. A further advantage attending the use of heated air, arises from the larger proportion of iron ore to fuel in the charge, and the consequent greater power of the contents of furnace to absorb heat from the ascending gas.

The heat generated when carbon is burnt to carbonic dioxide amounts to 8,000 heat units; but when carbonic oxide is produced the amount of heat generated is not quite one third, or 2,400 heat units, so that as regards heat-producing power the effect is the same as if only one third of the carbon in the fuel consumed had been converted into carbonic dioxide.

Taking the consumption of fuel in smelting iron ore to be equivalent to a quantity of carbon twice as great as that of the pig iron produced, the quantity of carbon that is converted into carbonic dioxide by the reduction of ferric oxide will amount to only one sixth of the whole. The heating effect produced by the remaining five sixths of the fuel consumed will be less than one third of that which it would produce if the product of combustion were carbonic dioxide. In other words, the only portion of the fuel consumed so as not to be further available as a source of heat is that equivalent to the reduction of the iron in the ore, supposing also the metal to be in the state of ferric oxide, the carbon thus consumed would be only about one third the weight of the pig iron obtained, and when the consumption of fuel is at the rate of two tons for the ton of pig iron, it will amount to only 16 per cent. of the fuel consumed.

Of the heat actually evolved in the smelting operation, a portion is absorbed in raising the temperature of the materials constituting the charge, and a further portion is rendered latent by the fusion of the slag and reduced iron, as well as by some of the chemical changes which take place; further portions are dissipated as sensible by conduction and radiation, by the heating of the tuyere water and heat carried off by the gas discharged from the furnace throat.

The rate at which the mixture of carbonic oxide and nitrogen ascends through the column of materials in the shaft of the furnace is determined by the rapidity of combustion and fusion at the tuyeres. As the gas comes in contact with the iron ore, reduction will take place, and a portion of the carbonic oxide will be converted into carbonic dioxide. There is, however, a considerable difference in the susceptibility of different ores to reduction. Consequently the reducing effect produced under conditions otherwise similar may be very much less in some cases than in others; and since the oxygen in the ore is a tolerably constant quantity per ton of pig iron, the way to ensure its separation from a difficultly reducible ore is to make the current of gas more rapid, or to increase the temperature of the region in which the reduction of iron ore takes place. The adoption of the former alternative involves the consumption of more fuel, and a proportionate increase in the amount of carbonic oxide in the gas discharged from the furnace. The latter alternative involves a possibility of the reconversion of carbonic dioxide into carbonic oxide by reaction with carbon of the heated fuel, a change which is attended not only with absorption of heat, but also with an excessive waste of carbon.

Most probably the reduction of the ferric oxide in the iron ore by reaction with the carbonic oxide in the ascending gas takes place progressively, and since it does not require a very high temperature it may extend for a considerable range in the descending column of materials, in proportion to the temperature prevailing and the amount of carbonic oxide in the gas.

When the iron ore smelted has not been previously calcined, and it contains carbonic acid or water, these substances will be separated during the descent of the charge in the shaft, and will mix with gaseous products of combustion. This will also be the case with the carbonic acid of the limestone used as a flux, and if coal be used as fuel its volatilisable portion will likewise be expelled and mix with the ascending gas. In proportion as the extent of this admixture is greater, the gas discharged from the throat of the furnace will have lower heating power when burnt, and therefore it is desirable to reduce the amount of carbonic acid and water vapour in the gas by previous calcination of the ore and limestone whenever the gas is to be used as fuel.

In all cases the essential conditions for securing economy of fuel are to reduce as far as possible the temperature of the gas before it is discharged, and to convert as much as possible of the carbon into the state of carbonic dioxide. By augmenting the capacity of the blast furnace and the height of the shaft, these effects have been produced to such an extent that the discharged gas has sometimes a temperature of only 190°, instead of 600° and upwards, as is the case in some furnaces. At the same time the calorific power of the fuel consumed has been realised to such an extent that the carbonic dioxide in the discharged gas amounts to nearly one-half the volume of the carbonic oxide associated with it, as shown in the following table:—

Locality	Height of shaft	Capacity of furnace	Relative volume of CO	Relative volume of CO^2
	feet	c. feet		
Ferryhill .	80	16,000	100	33·6
,, .	103½	33,000	100	34·9
Ormesby .	76	20,640	100	34·6
Consett . .	55	11,400	100	31·9
,, . .	55	10,300	100	40
Clarence . .	80	11,500	100	44·14
,, . .	80	25,500	100	40·3
,, . .	—	11,500	100	39·64
,, . .	—	15,500	100	35·4

The advantage of a large furnace with a high shaft may, according to Mr. Bell, be regarded as consisting in the removal of the region at which reduction of ferric oxide and carbon deposition takes place so far from the tuyeres that it never acquires a temperature high enough to induce the conversion of carbonic dioxide into carbonic oxide by combination with carbon. When that is done the furnace has reached the

dimensions necessary for working with the maximum of carbonic dioxide in the discharged gas, the least loss of sensible heat, and as a consequence with the minimum amount of fuel.

If these dimensions are exceeded, the result, so far as reduction and carbon impregnation are concerned, is the establishment of a region of neutral character in the furnace, which may probably be advantageous in securing regularity of action, but is of no value in altering the power of the gas to hold only a certain amount of carbonic dioxide.

If the operation can be carried on so that the whole of the carbonic dioxide arising from deoxidation of iron ore and carburation of the reduced iron escapes in the gas discharged from the furnace at a temperature of about 275°, the air does not require to be heated beyond 297° to ensure the greatest economy of fuel.

The use of hot blast also admits of a change in the relation between the solid and gaseous contents of the furnace that has the effect of accelerating the distribution of heat from the gas through the solid materials which are thus heated more rapidly while the gas is more fully saturated with oxygen in consequence of its longer retention in the furnace. Supposing, for instance, a furnace of 6,000 cubic feet capacity has supplied to it by means of hot air a quantity of heat equal to 6 cwts. of carbon over and above what it would receive if the air were driven in at the atmospheric temperature, the proportion of fuel in the charge could be reduced to that extent, and the result would be a reduction of the volume of gas flowing upwards through the contents of the shaft, equal to nearly ten per cent. of the volume the gas would have when cold blast is used and the consumption of fuel amounts to 60 cwts. per ton of pig iron. The carbonic oxide would therefore be retained one-tenth longer in the furnace, and it would have a greater opportunity of heating the solid contents of the shaft and absorbing oxygen from the iron ore.

As a general result of the experimental investigation carried out by Mr. Bell, it is inferred that the value of hot blast is in no way dependent on the increase of intensity of heat in the furnace, but that the differences in the amounts of fuel requisite for smelting different kinds of iron ore are due to the fact that the rate of reduction must be almost as rapid as the rate of fusion. The means by which economy of fuel is to be effected in accordance with this principle, are to increase the capacity of the furnace sufficiently to ensure the most perfect combustion of the fuel inside the smelting furnace, instead of having carbonic oxide outside the furnace and returning to it the heat so generated in the hot-air apparatus. The improvement on the consumption of fuel in certain cases by the use of hot blast, is therefore not so much due to the additional heat conveyed into the hearth of the smelting furnace as to the increase in the reducing energy of the furnace gas consequent upon the increased temperature to which the ore is raised in the upper portions of the shaft.

The following tabular statement of the result of analyses of gas taken from different heights in the shafts of blast furnaces will serve in some degree to illustrate the nature of the changes resulting from the chemical reaction taking place between the gaseous products of combustion and the solid materials contained in the shaft. The formation of carbonic oxide is probably one of the most important features of the smelting operation, since there is every reason to believe that the reduction of the iron ore is effected mainly, if not entirely, by this gas, aided perhaps in some instances by hydrocarbon vapour and gas produced from the fuel by the action of heat. In the immediate neighbourhood of the tuyeres, the oxygen of the air-blast becomes saturated with carbon immediately it comes into contact with the fuel at that part of the furnace. It is at this point that, while the fuel is being consumed, the reduced metal and the earthy substances mixed with it are melted, and, falling down into the hearth, make room for a fresh quantity of the material in the shaft of the furnace to sink down and undergo the same change, while the gaseous mixture of carbonic oxide and nitrogen ascends and communicates its heat to the materials in the upper part of the shaft.

The volume of the carbonic oxide, formed by the conversion of oxygen into carbonic oxide, is twice that of the oxygen consumed, and when carbon is burnt in this manner by atmospheric air, containing 21 per cent. of oxygen by volume, the gas produced will have the following percentage composition by volume:—

Carbonic oxide	34·71
Nitrogen	65·29
	100·

The ratio of oxygen to nitrogen in this mixture is 2658·1, the same as in atmospheric air. On reference to the table giving the composition of the gas in the smelting

Name of work, etc.	Depth below the mouth.	Percentage composition by volume							Ratio of oxygen to nitrogen
		N	CO	CO_2	H	C_2H_4	C_4H_6	CN	
	feet								
	5	55·35	25·97	7·77	6·73	3·75	0·43	—	0·374
	8	54·77	20·24	9·42	6·49	8·23	·85	—	·375
Alfreton;	11	52·57	23·16	9·41	9·33	4·58	·95	—	·418
Derbyshire.	14	50·95	19·32	9·10	12·42	6·64	1·57	—	·368
Fuel, coal.	17	55·49	18·77	12·43	7·62	4·31	1·38	—	·375
Hot blast 390°.	20	60·46	19·48	10·82	4·83	4·40	—	—	·340
Bunsen and Playfair.	23	58·28	26·97	8·19	4·92	1·64	—	—	·371
	24	56·75	25·19	10·08	5·65	2·33	—	—	·381
	34	58·05	37·43	—	3·18	—	—	1·34	0·322
	1	57·06	28·61	11·39	2·74	0·20	—	—	0·450
		56·64	28·93	11·39	3·04	—	—	—	—
Seraing;	4	59·64	28·06	9·85	0·97	1·48	—	—	—
Belgium.	9	62·46	33·88	1·54	0·69	1·43	—	—	—
Fuel, coke.	$9\frac{5}{6}$	61·67	35·20	1·08	1·72	0·33	—	—	0·301
Hot blast 100°.		61·15	35·35	1·13	2·08	0·29	—	—	—
	$11\frac{2}{3}$	61·34	36·30	0·10	2·01	0·25	—	—	—
	45	54·63	45·08	—	0·25	0·07	—	—	0·412
	3	62·34	24·20	8·77	1·33	3·36	—	—	0·334
	4·5	62·25	22·24	11·14	1·27	3·10	—	—	
Veckerhagen;	6	66·29	25·77	3·32	0·58	4·04	—	—	0·295
Hesse-Cassel.	7·6	62·47	30·08	3·44	1·77	2·24	—	—	0·285
Fuel, charcoal.	9	63·89	29·27	3·60	2·17	1·07	—	—	—
Bunsen.	12	61·45	26·99	7·57	0·15	3·84	—	—	—
	15	64·58	26·51	5·97	1·06	1·88	—	—	0·296
	9	64·43	8·04	22·20	1·46	3·87	—	—	—
Bärum;	12	62·65	15·33	18·21	2·53	1·28	—	—	0·413
Norway.	14	63·20	18·57	12·45	4·51	1·27	—	—	—
Fuel, charcoal.	17	64·28	29·17	4·27	1·05	1·23	—	—	0·293
Scheerer.	19	66·12	20·28	8·50	3·29	1·18	—	—	—
	22	64·97	26·38	5·69	2·96	—	—	—	0·290
	throat	57·79	23·51	12·88	5·82	—	—	—	—
Clerval;	3	57·80	22·24	13·96	6·00	—	—	—	0·434
France.	8	58·15	22·65	13·76	5·44	—	—	—	—
Fuel, charcoal.	12	59·14	28·18	8·86	3·82	—	—	—	0·387
Hot blast 175° to 190°.	16	60·54	33·64	2·23	3·59	—	—	—	—
Ebelmen.	$17\frac{1}{2}$	63·07	35·01	—	1·92	—	—	—	0·279
	tuyere	56·08	41·59	0·31	1·42	—	—	—	—
	$3\frac{1}{4}$	57·22	24·65	12·01	5·19	0·93	—	—	0·424
		58·56	23·85	11·95	4·31	1·33	—	—	—
Clerval;	$9\frac{5}{8}$	60·92	31·56	4·14	3·04	0·34	—	—	0·327
France.		60·89	31·34	4·23	2·77	0·77	—	—	—
Fuel, charcoal.	$19\frac{2}{3}$	63·04	35·05	0·49	1·06	0·36	—	—	0·206
Cold blast.		63·06	35·47	0·07	1·09	0·31	—	—	—
	$27\frac{5}{6}$	61·22	37·55	—	1·13	0·10	—	—	—
		58·17	39·86	0·93	0·79	0·25	—	—	0·359
	throat	55·62	25·24	12·59	6·25	—	—	—	0·453
Audincourt;	$11\frac{1}{2}$	54·39	23·62	14·46	7·53	—	—	—	—
France.	$14\frac{3}{4}$	56·07	28·82	9·55	5·56	—	—	—	—
Fuel, charcoal.	18	57·84	30·03	7·54	4·59	—	—	—	0·391
Hot blast 250°.	$21\frac{5}{6}$	57·87	34·28	3·81	4·04	—	—	—	—
	$26\frac{1}{6}$	61·61	36·39	0·21	1·79	—	—	—	0·298
	11	70·50	13·11	16·39	—	—	—	—	0·325
Wrbna;	17	71·36	10·89	17·80	—	—	—	—	—
Styria.	23	68·81	21·59	9·60	—	—	—	—	0·296
Fuel, charcoal.	27	66·66	30·66	2·68	—	—	—	—	0·270
Hot blast 200°.	34	66·34	20·06	11·60	—	—	—	—	0·327
Tunner.									

furnace, it will seem that even in the gas at the bottom of the furnace the oxygen it contains almost invariably exceeds this proportion. Mr. Bell is of opinion that this excess of oxygen in the gas at and near the level of the tuyeres is due partly to the formation of cyanogen and the reduction of alkalies accompanying the formation of alkaline cyanides, partly, also, to the reduction of silica, sulphuric oxide, phosphoric oxide, and probably lime: he also considers that a further addition of oxygen to the gas results from the presence of some oxygen in a state of combination with the spongy metal, which cannot be removed by the action of carbonic oxide, but only when the metal is undergoing fusion and the finely divided carbon mixed with the spongy metal reacts with the oxidised portion. The following tabular statement of the relative quantities of carbon, oxygen, and nitrogen in the gas at different levels of the smelting furnace, as deduced from the foregoing analysis, will show clearly the extent to which there is a variation in the ratio of oxygen to nitrogen by volume.

	N	O	C
	Clerval.		
throat	57·79	24·63	36·39
3 feet	57·80	25·08	36·30
8 ,,	58·15	25·08	36·41
12 ,,	59·14	22·95	37·04
16 ,,	60·54	19·05	35·87
	63·07	17·50	35·01
1½ above tuyere	56·08	21·10	41·90
	Clerval.		
3¼ feet	57·22	24·33	36·66
9¾ ,,	60·92	19·92	35·70
19¾ ,,	63·04	18·01	35·54
28 ,,	61·22	18·77	37·55
at tymp	58·17	20·86	40·79
	Wrbna.		
11 feet	70·50	22·94	29·50
17 ,,	71·36	23·24	28·69
23 ,,	68·81	20·39	31·19
27 ,,	66·66	18·01	33·34
at tuyeres	66·34	22·63	33·66
	Seraing.		
1	57·06	25·69	40·00
4	59·64	23·88	37·91
9	62·46	18·48	35·42
10	61·67	18·68	36·28
11¾	61·34	18·25	36·40
near tuyeres	54·63	22·52	45·05

It is also evident from these data that at some distance above the level of the tuyeres the amount of carbon in the gas is less in proportion to the nitrogen than it is at a lower level. This reduction in the amount of carbon is probably due to deposition of carbon by the decomposition of carbonic oxide, which takes place simultaneously with the reduction of ferric oxide, and appears to be a very important feature of the action taking place in the smelting furnace. The temperature at which the elimination of carbon takes place is, according to Mr. Bell, between 399° and 455°, and it accompanies the reduction of ferric oxide by carbonic oxide. The carbon thus eliminated appears to be diffused throughout the mass of the iron ore undergoing reduction, and this absorption of the carbon is attended with a considerable disintegration of the iron ore, to such an extent that it is often converted into a black pulverulent mass.

Manufacture of Malleable Iron.—There are two methods by which iron may be produced in such a state as to be capable of being wrought by hammering or rolling. According to the one method, which was formerly the only one adopted, the metal is obtained by heating a suitable iron ore in contact with charcoal burning under the influence of a blast of air, as in a smith's forge. The reduction of the iron in this case is probably effected entirely by carbonic oxide, and since the temperature is not high enough to determine the carburation of the metal to such an extent as is requisite for the formation of cast iron, the reduced iron is obtained in the state of a coherent spongy mass, termed a bloom, which is then rendered compact by hammering it while red hot so as to weld or unite together the particles into one mass. Only the richer kinds of iron ore can be worked in this way, and even with such ore the production of

malleable iron by the direct method is always attended with very considerable waste, since a large portion of the metal escapes complete reduction and, in the state of ferrous oxide, combines with the silicious and earthy portions of the ore, giving rise to the production of a readily fusible slag consisting chiefly of ferrous silicate.

The other method, by which malleable iron is now chiefly produced, consists in operating upon fusible carburetted pig iron in such a way as to deprive it of the greater part of the carbon and silicon it contains. This is in all cases effected by a partial oxidation of the pig iron, the excess of carbon being burnt together with the silicon, while a portion of the iron is at the same time oxidised. A fusible slag consisting of ferrous silicate is thus formed, which reacts upon the remaining carburetted iron, oxidising and separating a further portion of the carbon, as well as other substances which are frequently present in pig iron and would be prejudicial to the quality of malleable iron.

The production of malleable iron by the direct method is chiefly practised according to what is termed the Catalan method, which consists in heating the roasted ore in a charcoal fire urged by a blast in a manner very similar in its general character to that adopted in working a smith's forge. The most important part of the arrangement for this operation is the hearth, which is a nearly cubical chamber built of stone and lined with slabs of iron (*s s t t*, fig. 398) at the back and front. The hearth is placed against a wall (N N) through which the tuyere (T) of the blowing machine projects into the hearth. The ore to be reduced is broken into pieces the size of a nut and placed against the front of the hearth (*s s*), while the remaining space (M) is filled with charcoal, and when the hearth is filled in this way the upper part of the heap of ore forms a ridge (*d f g*) the surface (*f g*) being covered with a layer of closely packed charcoal dust. The fire is then urged by the blast and the ore becomes gradually deoxidised, while the gangue, or earthy substance contained in the ore, combines with a portion of ferrous oxide, forming a fusible silicious slag which runs down to the bottom of the hearth. Fresh charcoal and finely divided ore are constantly supplied to the fire meanwhile, and eventually the deoxidised metal sinks down in a pasty condition to the bottom of the hearth where the fragments are worked together by a workman into a spongy mass, which is taken from the fire and rendered solid by hammering while still red hot, so as to crush the metallic particles; it is then drawn out into bars under a forge hammer.

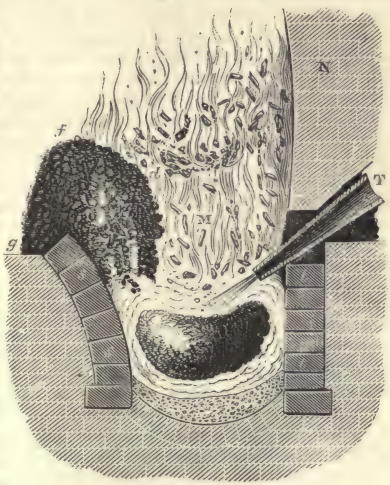


FIG. 398

In the reduction of iron ore by this method the consumption of fuel is very considerable, and, as charcoal must be employed, it can only be practised in districts where wood is very abundant and cheap. This mode of making malleable iron is now almost entirely abandoned in Europe, but in some parts of America it is still adopted, though less extensively than it was at one time.

A variety of other methods of producing malleable iron direct from iron ore have been proposed from time to time; thus, for instance, Chenot subjected a mixture of brown hematite or other rich ore with charcoal to a high temperature in close chambers heated externally, and thus obtained spongy metallic iron which was afterwards welded together into a compact mass. Gurlt endeavoured to effect the reduction of iron ore by heating it in an atmosphere of carbonic oxide, and afterwards to obtain the metal in a compact state by welding.

At a later period Siemens endeavoured to produce malleable iron direct from the ore by dissolving the spongy metal in melted pig iron. In the first instance the iron ore was reduced by heating it with charcoal in vertical cylinders heated externally, but as the expenditure of fuel was too large, a rotating chamber was tried in the interior of which the mixture of charcoal and iron ore was heated by the flame of gaseous fuel, and the spongy metal was delivered into a bath of melted pig iron until so much of it had been dissolved as to produce malleable iron. It was, however, found that as the spongy metallic iron absorbed sulphur, the production of good iron by this mode of working could not be accomplished.

A further improvement consisted in first melting the iron ore with suitable fluxes and then stirring up the liquid mass with sufficient carbonaceous material to precipitate metallic iron in a compact state while the earthy constituents of the ore formed a fusible slag. It was found that the reduction of iron in this way could be accomplished only at a very intense heat far exceeding the welding heat of iron, but the iron so produced was very pure, even when there were considerable amounts of sulphur and phosphorus in the ore and the fuel used.

The operation is carried out in a rotating cylindrical chamber lined with a very refractory material made of bauxite mixed with some fire clay. This cylindrical chamber is mounted on friction wheels and fitted with wheel gearing, so that it can be made to revolve about once in a minute, and thus mix the ingredients of the charge operated upon. At the same time a mixture of gaseous fuel and air is supplied to the chamber to keep up a sufficiently high temperature, and when the reduced iron assumes the form of balls, it is taken out and shingled in the usual manner.

The production of malleable iron by the indirect method is conducted in three different ways, either by heating pig iron in an open hearth or forge, termed a finery, or in a reverberatory furnace, and, while it is in a partially fused pasty condition, admitting sufficient access of atmospheric air to effect the requisite degree of oxidation; or by submitting melted pig iron to the action of a current of atmospheric air, forced through it until a sufficient degree of decarburisation is effected. When the open hearth is employed the fuel used is generally charcoal, and this method of producing malleable iron is therefore termed the charcoal finery. When the reverberatory furnace is used, the operation is termed puddling, and the third method of forcing air into melted pig iron, recently introduced by Bessemer, is termed converting.

The main distinction between the treatment of pig iron in the charcoal finery and in reverberatory furnaces is that in the former case charcoal is employed as fuel, and in contact with the pig iron operated upon, while in the latter case the iron is acted upon in a separate chamber without actual contact with the fuel, so as to admit of coal being used.

For the production of malleable iron in this way white pig iron containing but a small amount of carbon is most suitable, because in melting it does not become so liquid as grey pig iron, but acquires a viscous condition which admits of its being stirred about so as to present a greater extent of surface to the oxidising influence of the air. Moreover, the carbon existing in a state of chemical combination in white pig iron is oxidised much more readily than the graphitic carbon in grey pig iron.

The production of malleable iron in the charcoal finery is carried out in different localities with a great variety of modification in the details of manipulation, some of which are determined by special peculiarities in the nature of the material operated upon, while others depend upon less important circumstances.

The hearth and its accessories are generally constructed in the manner represented by figs. 399 and 400. The vertical section fig. 399 shows the hearth (D) lined with iron

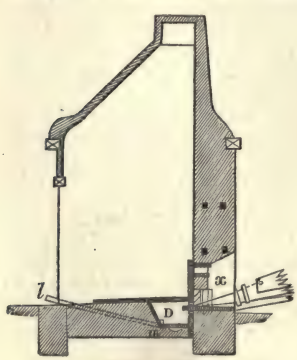


Fig. 399.

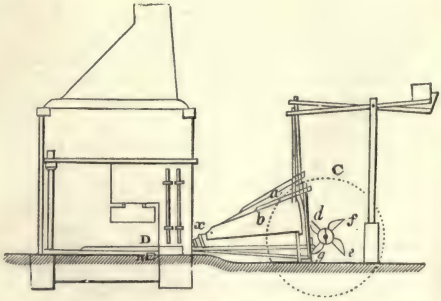


Fig. 400.

slabs two or three inches thick, the bottom plate having a cavity (*m*) beneath it into which water can be run through the tube (*l*), when it is desirable to cool the contents of the hearth, and hasten the solidification of the iron. The blast of air is furnished by means of bellows (*a b*) as in a smith's forge, and they are often worked by a water-wheel (c) driving a shaft carrying canes (*d, f, e g*). At the back of the hearth there is an arched opening (*x*) in the wall supporting the hood, and through that opening the

tuyeres of the bellows are fitted so as to deliver the air at a suitable angle into the hearth.

The pig iron is melted above the tuyere, so that it may not be exposed to the action of the blast until it is melted, and it is then kept in a proper state of fusion by regulating the blast. At intervals the blast is stopped, and after the slag has been run out of the hearth, the mass of metal is lifted up from the bottom and a fresh supply of charcoal placed beneath it. When the consistency of the metal indicates that the decarburation has been carried far enough, the mass is again raised up, covered over with charcoal, and subjected to a strong welding heat by which the adhering slag is melted and detached, while the iron is brought to such a temperature that it can be hammered into a compact lump or bloom.

During the first stage of the operation, a slag is produced which is readily fusible and very liquid, but solidifies rapidly, forming a blackish-grey crystalline mass of metallic lustre and frequently iridescent. Notwithstanding the crystalline structure of this slag, it is sometimes porous. Chemically it presents some analogy to olivine not only in its composition, as shown by the following analyses, but also in its general characters and the crystalline form it sometimes presents.

Analyses of Poor Slags from the Charcoal Finery.

	Mitscherlich	Rammelsberg	Walchner	Wiegand	Dugendt	$2FeO.SiO_2$
Ferric oxide	—	2·25	—	—	0·74	—
Ferrous oxide	67·24	63·51	62·04	57·3	65·83	70·59
Manganous oxide	—	—	2·64	4·5	—	—
Magnesia	0·65	—	1·40	—	—	—
Lime	—	—	—	2·8	—	—
Alumina	—	—	—	3·0	—	—
Potash	—	—	0·28	—	—	—
Silica	31·16	34·38	32·34	32·4	33·47	29·41
	99·05	100·14	98·70	100·0	—	—
Percentage of iron	52·30	50·69	48·25	44·95	—	—

The slag formed towards the end of the operation is less liquid than that just described; but it does not solidify so rapidly, and forms an agglutinated mass of iron-grey colour, considerable density and compact fracture. The composition of this slag varies very much, as shown by the analyses given in the following table, and the later the period at which it is formed the higher is the amount of iron it contains. In some instances this slag may contain a compound of ferric oxide with ferrous oxide, together with a basic silicate $3FeO.SiO_2$, the percentage composition of which is 78·26 ferrous oxide and 21·74 silica.

Analyses of Rich Slag from the Charcoal Finery.

	Winckler	Sefström	Lampadius	Berthier	Ström	Karsten	Hoffmann
Ferric oxide	—	—	—	—	—	—	6·00
Ferrous oxide	82·9	82·1	77·00	74·0	71·3	61·2	71·15
Manganous oxide	—	6·8	3·00	3·6	—	6·7	—
Magnesia	3·2	2·8	—	—	2·7	2·4	0·46
Lime		—	1·75	1·8	—	0·9	1·26
Alumina		—	3·00	1·2	—	0·2	—
Potash		—	—	—	—	—	—
Silica	13·9	7·6	10·25	19·8	21·4	18·1	21·01
Phosphoric acid	—	—	1·75	—	3·7	—	—
	100·0	99·3	96·75	100·4	99·1	89·5	99·88
Percentage of iron	64·48	63·86	59·89	57·56	55·46	47·6	59·50

In addition to the two kinds of slag produced in making malleable iron by the charcoal finery method, a further portion of the metal is converted by oxidation into magnetic oxide which, in the form of forge scale, coats the blooms while they are

being taken from the hearth and welded together or hammered out. In order to reduce the waste of metal, this scale is added to the charge in subsequent operations, and it serves to promote the decarburation of the pig iron.

In the production of malleable iron by this process, the separation of carbon, silicon, phosphorus and manganese from the pig iron is effected by the oxidation of these substances, partly by the direct action of atmospheric air and partly by the ferric oxide and ferrous oxide in the slag formed towards the end of the operation. When carburetted iron is heated in contact with ferric oxide or magnetic oxide of iron they yield carbonic oxide gas and metallic iron. Under the same conditions silicide of iron yields normal ferrous silicate which forms slag, but this substance is not decomposed when heated to redness in contact with carburetted iron or with carbon, and it is only at a very high temperature that any reaction takes place resulting in reduction of the iron. However, the basic ferrous silicate contained in the slag formed at a later stage of the operation is decomposed even at a red heat by carburetted iron, and while the excess of ferrous oxide in the slag is reduced to the metallic state, carbon is abstracted from the pig iron.

When the pig iron is first melted down in the hearth, normal ferrous silicate is formed, partly by the oxidation of silicide of iron in the pig, and partly also by the combination of ferrous oxide with silica derived from the ashes of the fuel and from sand adhering to the metal. The slag thus produced takes up the ferrous oxide continually formed by the oxidation of the metal, gradually becoming richer in iron, and in this state it acts as an oxidising agent upon the carbon of the pig iron, at the same time any manganese or phosphorus present in the pig iron is also oxidised and taken up by the slag as manganous oxide and phosphoric acid.

The conversion of pig iron into malleable iron by this method must not be carried on too rapidly, or the oxidation of the silicon, phosphorus, etc. will not be complete, and consequently the decarburised iron will be impure. This is especially the case with the less pure varieties of pig iron. But it is equally important that the operation should not be protracted so far as to cause unnecessary waste of iron by oxidation. In all cases this waste is considerable, since much more iron is oxidised than is requisite for effecting the chemical changes that take place and the malleable iron obtained does not on the average amount to more than from 70 to 75 per cent. of the pig iron operated upon. The waste is less in working white pig iron than in working grey pig iron, which is more liquid when melted, and less readily decarburised.

The charcoal finery employed in South Wales for the production of a superior kind of iron suitable for the manufacture of tin plate is represented by fig. 401. It consists of a rectangular hearth formed of cast-iron slabs, set in brickwork. The bottom slab is cast hollow in order that it may be kept cool by the circulation of a current of air through it while the hearth is being worked. The hearth is enclosed within brick walls, and the waste gas from the fire is carried off by a chimney. Sometimes the pig iron is heated by this gas, or even melted in a separate furnace before it is introduced into the finery, the object being to economise fuel and to expedite the operation. The charcoal finery is now constructed of larger dimensions than formerly, and the pig iron is first run down under coke so as to obtain it in the state of white pig iron, which is decarburised by heating it with charcoal in the finery hearth. When the charge of metal becomes sufficiently malleable, it is worked under a hammer into a slab-shaped mass called a stamp, which is then broken into pieces, and a number of them piled upon a kind of shovel are raised to a welding heat in the centre of a mass of ignited charcoal; the pile is then again hammered into slabs, which are reheated, cut up, and rolled, first into bars and then into sheets of the size and thickness required.

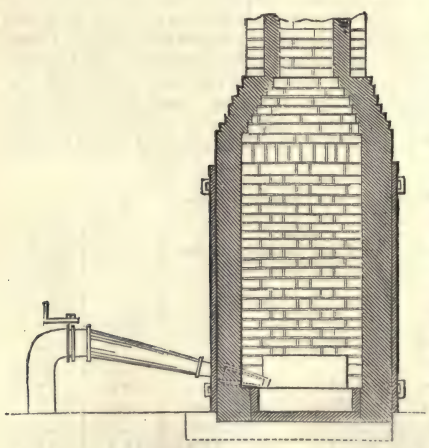


FIG. 401.

The fuel employed in producing malleable iron from pig iron in this way is almost always charcoal, and the operation is essentially of the same nature as that already described as being carried out in various parts of the continent, the superior character

of the metal produced and known as charcoal iron being in all cases chiefly due to the purity of the fuel employed.

The Lancashire hearth or charcoal finery is represented by figs. 402 and 403. The hearth is a shallow quadrangular space formed of cast-iron plates (*a b c e*, fig. 403).

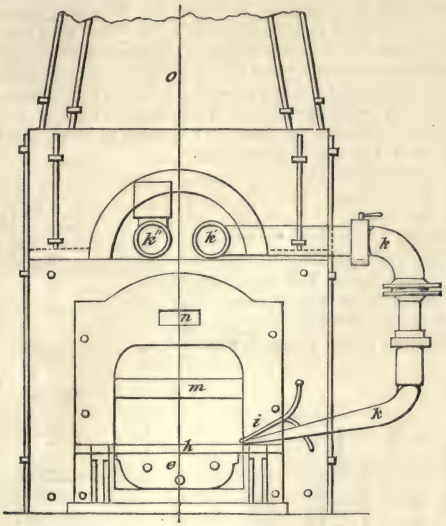


FIG. 402.

Under the hearth is an open shallow cast-iron box having a gutter (*f*) on one side, and a round hole in the centre, the sides of which are raised so that water may be kept in the box when the furnace is working. Hot blast is used in the operation, and the pipes (*k' k''*) for heating the air are arranged in the flue by which the product of combustion, escaping through the opening (*l*) is carried off into the chimney (*o*). By means of the pipe (*i*) attached to the tuyere box a current of water is made to circulate within the box so as to protect it from the influence of the heat where it projects into the hearth.

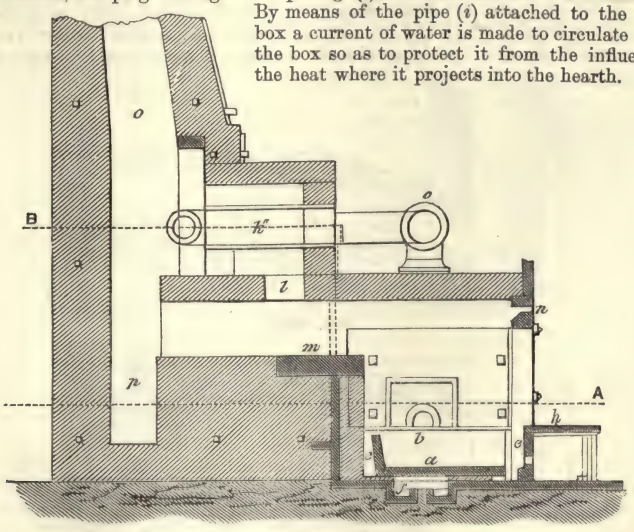


FIG. 403.

The cast-iron plate (*m*) is for heating the blooms, and a cast-iron platform (*h*) is fixed in front of the hearth. The opening (*n*) serves for the introduction of an iron bar for cleaning the flue.

The substitution of a reverberatory furnace for the open hearth in the production of malleable iron from pig iron was attempted with the object of using coal in the operation, and the introduction of this system by Cort in 1784 was one of the most important epochs in the history of the iron trade. The chief point in which this method of puddling differs from that of the charcoal finery is the decarburation of the pig iron in a chamber separated by a wall or fire bridge from the furnace in which the fuel is burnt. The metal is thus kept out of contact with the fuel, and is acted upon only by the flame and hot gaseous product of combustion, passing over the fire bridge into the chamber containing the iron. By this arrangement the contamination of the iron with the impurities always present in coal is prevented.

The construction of a puddling furnace is represented by figs. 404, 405, and 406, in elevation, vertical and horizontal sections. It is built of brick and cased with strong plates of cast iron held together by iron bars. The fire place (*bb*) is shown in the sections, and at one side of it is the firing hole (*a*); it is separated by the fire bridge (*c*) from the bed of the working chamber (*f*), and the arched roof of this chamber dips down at the end next to the chimney (*i*) so as to bring the flame from the fire place into contact with the pig iron. The bed or hearth (*d d*) of the working chamber is constructed of cast-iron plates covered with a

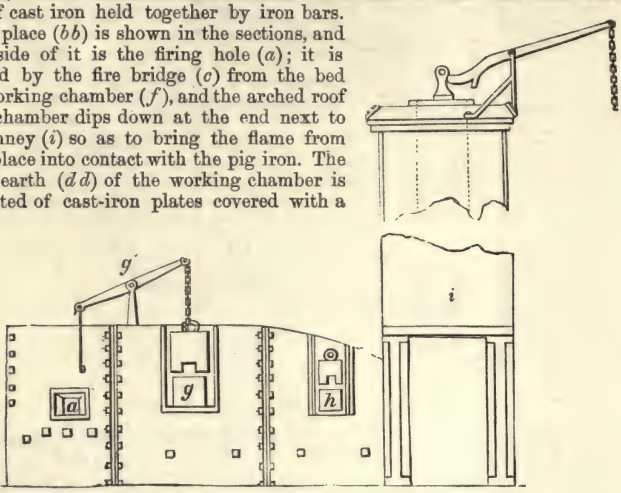


FIG. 404.

layer of red iron ore, or some other material consisting chiefly of ferric oxide. The working door by which the opening (*g*) is closed has a small hole at the bottom through which an iron tool is passed for the purpose of stirring the melted metal.

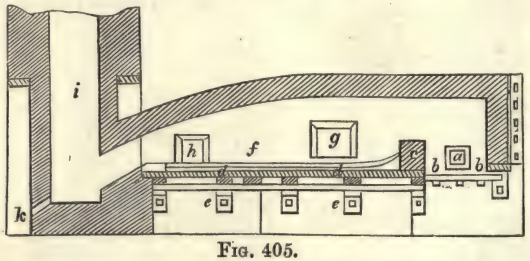


FIG. 405.

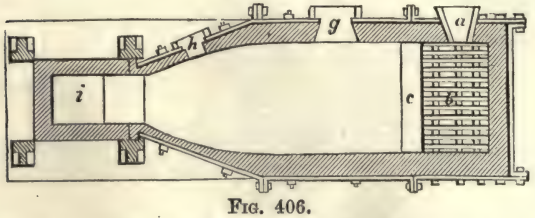


FIG. 406.

Just below the door and level with the surface of the hearth is a small hole called the floss or tap hole, that can be closed with a plug, and through which the slag formed on the hearth is run out at intervals. Sometimes the slag is allowed to run

away through a hole (*k*) below the chimney. The door (*h*) serves for introducing a fresh charge of pig iron into the puddling chamber. The chimney (*i*) is generally from 30 to 50 feet high, and it is furnished with a damper at the top for regulating the draught, as shown by fig. 404.

The chemical changes that take place in the production of malleable iron by puddling are essentially the same as those already described under the head of the charcoal finery, the decarburation being effected by the joint action of the atmospheric air passing through the working chamber, and of materials capable of yielding oxygen, such as basic ferrous silicate, forge scale, ferric oxide, etc.

In the production of malleable iron by puddling, oxidation takes place by the direct action of atmospheric air more readily than in the charcoal finery, since the melted pig iron on the bed of the puddling chamber exposes a larger surface, and it is more readily stirred about than in a hearth; but the reaction of basic ferrous silicate and other ferruginous materials capable of yielding oxygen to the pig iron is also of considerable importance, and in order to promote this reaction, it is requisite to maintain a constant intermixture of the pasty iron with the liquid slag. By the addition of hammer scale or powdered hematite at intervals, the slag is rendered more basic and of a pasty consistency, and on subsequently raising the heat, the evolution of blue flames of carbonic oxide indicates the progress of the decarburation.

Under the influence of the free oxygen in the atmosphere of the puddling chamber, a portion of the iron is oxidised, and at the same time the carbon, silicon, sulphur, phosphorus and manganese present in the pig iron are gradually oxidised, either by the direct action of atmospheric oxygen or by reaction with the ferruginous oxides added to the pig iron and formed during the operation. As a result of this oxidation a slag is produced consisting of ferrous and manganous silicates, together with magnetic oxide of iron and the various earthy impurities present in the pig iron operated upon, as well as part of the sulphur and phosphorus it contained, the one probably in the state of sulphide and the other as phosphate.

Another mode of conducting this operation is sometimes practised under the name of pig boiling, the distinctive characteristic of which is that the decarburation of the pig metal is effected more by the action of a slag consisting of basic ferrous and manganous silicates than by the direct action of atmospheric oxygen. In this case the bed of the working chamber is made deeper, so that the pasty mass of pig iron is immersed in a bath of the liquid slag, and considerable quantities of materials containing ferruginous oxides are added, together with some roasted slag from a previous operation.

In that modification of the method of producing malleable iron known as pig boiling, the pig iron does not undergo any preliminary treatment, and the furnace is sometimes charged with liquid metal run in direct from the smelting furnace so as to save the fuel requisite for remelting it. But in puddling the practice is generally to submit the pig iron beforehand to an operation known as refining, which consists in melting the pig iron in contact with coke and with the aid of a blast, in a hearth some what similar to a charcoal finery, but of larger dimensions, and termed a refining or running out fire. This operation has the effect of partially decarburising the iron and removing from it the greater part of the silicon, corresponding in fact to the first melting of the pig iron under the blast in the charcoal finery operation.

At the same time grey pig iron is brought into the condition of white pig iron, which is more suitable for conversion into malleable iron by puddling. This change is facilitated by suddenly cooling the metal with water as it runs from the hearth of the refinery.

The following analyses of refined iron, technically termed metal, serve to show its composition as well as the changes effected by this treatment.

	Dick	Abel		Noad		Regnault	
		pig iron	refined	pig iron	refined	pig iron	refined
Iron . . .	95·14	—	—	—	—	97·8	92·3
Carbon { combined .	3·07	—	—	—	0·30	1·7	3·0
Carbon { graphitic .	—	—	—	2·40	—	—	—
Silicon . . .	0·63	4·66	0·62	2·68	0·32	0·5	4·5
Sulphur . . .	0·16	0·04	0·30	0·22	0·18	—	—
Phosphorus . .	0·73	0·56	0·50	0·13	0·09	—	0·2
Manganese . .	trace	—	—	0·86	0·24	—	—
	100·	100·00	100·00	100·00	100·00	100·0	100·0

The construction of a refinery or running out fire is represented by figs. 407 and 408. It consists of a rectangular hearth (H) about 2 ft. deep, formed of cast-iron plates set upon a stone bed and arranged in such a way as to make a hollow space for water to circulate round the interior, as shown in the vertical section, fig. 407. The chimney (C) is

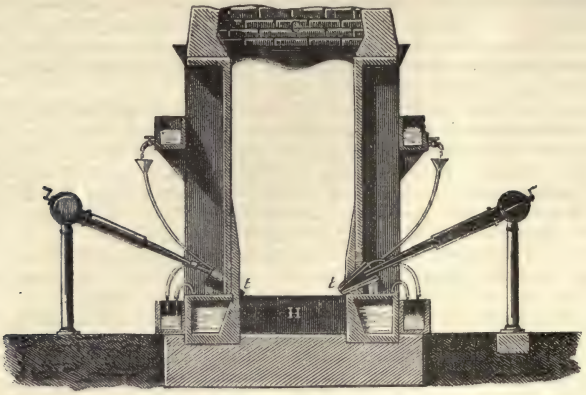


Fig. 407.

supported upon cast-iron columns, and the spaces between them are closed with cast-iron plates. On each side of the hearth are three blast tuyeres (*t t t*) connected with a blowing apparatus. At one end of the hearth is a tapping hole, through which the

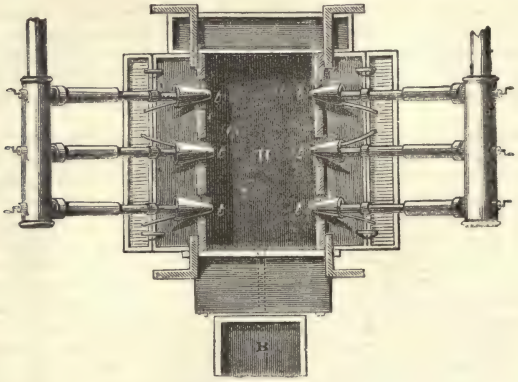


Fig. 408.

contents can be let out as desired into the square mould (B), where the refined metal solidifies in the shape of slabs.

When the pig iron is not run into the hearth of the refinery direct from the smelting furnace, it is piled up in the hearth upon a bed of ignited coke, and after being covered with more coke, the blast is turned on to accelerate the combustion until the whole of the pig iron has melted and run down upon the hearth. Under the oxidising influence of the blast the carbon and silicon in the pig iron are separated, and a slag consisting of ferrous silicate is produced which floats upon the surface of the liquid metal. Fresh fuel is then added and the heat is maintained until the purification of the metal has been carried far enough. The tap hole at the end of the hearth is then opened and the refined metal is run into the mould (B), where water is thrown upon it until it solidifies and the slag can be detached from the surface of the mass.

In addition to the partial decarburation of pig iron, and the separation of its silicon by the operation of refining, the sudden solidification of the metal has the effect of preventing the carbon from separating in the graphitic state, and the whole of it remains in combination. The product is therefore in the state of white cast iron, and

there is a considerable advantage in this for the puddling treatment, since the combined carbon is more readily oxidised than when it is in the graphitic state.

The slag produced in the operation of refining is vitreous and dark coloured. It consists essentially of ferrous silicate, and generally contains greater part of the manganese present in the pig iron operated, as well as some of the phosphorus and sulphur, together with the ash of the coke used as fuel. The composition is shown by the following analyses:—

	Stourbridge	Dowlais		Bromford
	Rammelsberg	Riley		Forbes
Ferric oxide	13·09	—	—	—
Ferrous oxide	73·22	65·52	54·94	61·28
Manganous oxide	—	1·57	2·71	3·58
Alumina	—	3·60	5·75	7·30
Lime	—	0·45	1·19	3·41
Magnesia	—	1·28	0·50	0·76
Silica	13·69	25·77	33·33	22·76
Sulphur	—	0·23	—	0·46
Ferrous sulphide	—	—	0·17	—
Phosphorus	—	1·37	0·99	—
Copper	—	—	trace	—
	100·00	99·79	99·68	99·55
Percentage of iron	66·11	50·96	42·84	47·66

In working the puddling process, the pig iron to be decarburised is piled up on the hearth of the working chamber, and when it begins to melt some oxidised material in the shape of hammer scale is added. The pasty metal is then broken up and stirred with an iron rabble worked through the small hole in the door (*g*, fig. 404). This operation is continued until the whole mass is reduced to a kind of sandy half-melted condition. The heat is then increased, and soon after the whole of the metal is melted, it begins to swell and heave as if boiling, while jets of blue flame issue from all parts of the mass. These are due to the combustion of the carbonic oxide produced by the reaction of the carburetted pig iron with the ferruginous oxides present. As this reaction progresses the metal becomes pasty, and in consequence of the oxidation of silicon in the pig iron, and the formation of ferrous silicate, a liquid slag separates from it, and collects upon the hearth.

The following analyses of slag from puddling furnaces will give an idea of the general composition of this product, which is commonly known by the name of tap cinder. It will be evident from these analyses that in the operation of puddling, phosphorus is removed to a considerable extent.

	Chillington	Dowlais		Bromsgrove	Bromford	Wales
	—	Riley		Percy		Noad
Ferric oxide	16·42	13·53	8·27	17·00	23·75	17·11	—
Ferrous oxide	60·14	57·67	66·32	58·67	39·83	48·43	70·48
Manganous oxide	2·29	0·78	1·29	0·57	6·17	1·13	12·80
Alumina	trace	1·88	1·63	2·84	0·91	1·28	—
Lime	0·70	4·70	3·91	2·88	0·28	0·47	—
Magnesia	0·42	0·26	0·34	0·29	0·24	0·35	—
Silica	15·30	8·32	7·71	11·76	23·86	29·60	8·24
Iron sulphide	—	7·07	—	3·11	0·62	1·61	—
Sulphur	trace	—	1·78	—	—	—	0·53
Phosphoric acid	4·66	7·29	8·07	4·27	6·42	1·34	7·66
Copper	—	trace	trace	—	—	—	—
	99·93	101·50	99·32	101·39	102·08	101·32	99·71
Percentage of iron	58·26	58·04	57·37	47·61	47·60	44·22	54·81

When the separation of carbon from the metal has advanced to some considerable extent, the oxidising action of the atmosphere in the working chamber is lessened by lowering the damper at the top of the chimney and keeping the iron surrounded by highly carbonised or smoky gas. After this condition has been maintained some time, and the iron has become malleable, or as it is termed 'come to nature,' the fragments are gathered together by means of an iron bar and worked into lumps, which are lifted out of the puddling chamber and consolidated by hammering.

The elimination of sulphur or phosphorus from pig iron appears to be always necessarily attended with oxidation of the metal in a degree proportionate to the quantity of those substances separated. Consequently it is essential that the amount of those substances in the pig iron operated upon should not be large, in order that the waste of metal thus incurred in producing malleable iron of good quality may not exceed such a limit as would be tolerable in practice. The smaller the amount of phosphorus and sulphur in pig iron, the more readily is it convertible into good malleable iron; and so far as the separation of those substances is concerned, the smaller is the necessary waste incurred in the operation.

The presence of sulphur in pig iron retards the conversion into malleable iron, and in the case of pig iron that is very liquid when melted, there is greater difficulty in bringing the metal into the plastic condition requisite for puddling than when it has a viscid consistency in the melted state, like good white pig metal containing a small amount of carbon and but little sulphur.

The manganese frequently present in pig iron is generally separated almost entirely in the manufacture of malleable iron by puddling. A certain proportion of manganese in the pig iron appears to exercise a beneficial influence upon the quality of the malleable iron produced from it by the operation of puddling, but the precise nature of this influence and the mode in which the manganese acts are still imperfectly understood. Caron's experiments led him to the conclusion that the presence of manganese promoted the separation of sulphur during the decarburation, but that it was not similarly effectual in causing separation of phosphorus. By melting sulphuretted pig iron, containing 1·15 per cent. of sulphur, three times without any admixture, the amount of sulphur was reduced to 0·96 per cent.; by adding to the pig iron 6 per cent. of metallic manganese, and then melting the alloy three times with access of air, the amount of sulphur was reduced to 0·8 per cent. The same pig iron melted with 10 per cent. of ferric oxide showed a reduction in the amount of sulphur from 1·15 to 1·08 per cent., and by melting the alloy of pig iron containing 6 per cent. of metallic manganese with 10 per cent. of ferric oxide, the sulphur was reduced to 0·07 per cent.

The separation of silicon from pig iron takes place very readily in puddling, as in other modes of producing malleable iron, under the influence of oxidation, the result being formation of a readily fusible ferrous silicate. The chief importance attaching to the presence of this substance in the pig iron employed for conversion into malleable iron relates more to the amount of malleable iron obtainable than to any special difficulty in the elimination of silicon. In the ferrous silicate constituting the slag of the puddling furnace there is three and a half times as much iron as silicon, so that if both the silica and the ferrous oxide of the slag originate from the oxidation of the pig iron operated upon, the waste of iron in this way will be considerable if the amount of silicon in the pig iron be large. Assuming that the slag is derived entirely from the pig iron by oxidation, the presence of 5 per cent. of silicon would be attended with a loss of 17·5 per cent. of iron due to that cause alone, independently of the loss resulting from the separation of carbon, silicon, and other substances. Hence it is very desirable that the amount of silicon in pig iron intended for conversion into malleable iron should not be very large.

The proportion of slag produced in puddling depends very much upon the kind of pig iron operated upon. Grey cast iron and unrefined pig iron containing a considerable amount of carbon furnish more slag than refined metal, the slag from which is relatively richer in ferrous oxide, and being consequently less fusible than the slag formed from grey cast iron it accumulates upon the bottom of the hearth in a thick layer and may sometimes contain an admixture of ferric oxide formed by the oxidation of the basic ferrous silicate or of the ferrous oxide produced in excess of that requisite to combine with the silica and form ferrous silicate.

The temperature to which iron requires to be heated in the operation of puddling may be expressed as corresponding to 1650°C., and assuming that the specific heat of cast iron augments above 350°C. in the same ratio that it does up to that temperature, it would be about 0·26 at 1650°, so that in this case the quantity of heat requisite to raise the temperature of a pound of iron to that extent above 16°—the average atmospheric temperature—would be 424·84 heat units.

$$1650° - 16° \times 0{\cdot}26 = 424{\cdot}84.$$

A further quantity of heat is consumed in melting the pig iron, which may be assumed as equal to 30 heat units, making the total heat requisite to raise the temperature of the iron up to 1650° and to melt it, equal to 454·84 heat units, and the quantity requisite for one ton of pig iron 1,018,841 heat units.

Taking the average calorific power of coal to be 7,778 heat units, it appears therefore that the quantity of heat actually communicated to the ton of iron in the operation of puddling is not more than that capable of being generated by 131 pounds of coal

$$131 \times 7{,}778 = 1{,}018{,}918.$$

The consumption of coal in puddling iron may, however, be taken as equal to the weight of pig iron worked, so that out of every ton of coal consumed in the puddling furnace, only 131 pounds, or not more than one-sixteenth part, is really effective in heating the iron. But though the quantity of heat actually communicated to the iron bears only this small proportion to the whole quantity generated by the combustion of the fuel used, it must be remembered that under existing circumstances, this large consumption of fuel is unavoidable, since it is indispensable that during the whole of the operation the temperature should be maintained sufficiently high to keep the iron melted or in a pasty condition. For this purpose the rate of combustion must be rapid, and the intensely heated product of combustion must pass rapidly through the working chamber of the furnace. The quantity of heat thus carried away in the gas passing off to the chimney is very large. It has been estimated that in the ordinary puddling furnace, when the consumption of coal is at the rate of 240 pounds per hour, the volume of heated gas passing through the working chamber amounts to upwards of 72 cubic feet per second, or sufficient to fill the working chamber twice in that time, and this rapid flow of gas is requisite in order to counteract the influence of conduction and radiation in reducing the temperature of the working chamber.

It is in consequence of the necessity for maintaining an extremely high temperature in the working chamber of the puddling furnace that only so small a fraction of the heat generated by combustion of the fuel consumed is really effective in heating the iron, inasmuch as it is only the heat corresponding to the difference existing at any moment between the temperature of the iron and the higher temperature of the atmosphere in the working chamber of the furnace that is available for maintaining or raising the temperature of the iron. So long, therefore, as the temperature of the iron in a puddling furnace requires to be 1650°, the gas passing into the chimney must be at a temperature not less than that, and the whole of the heat corresponding to the quantity of gas discharged at that temperature into the chimney will be without other useful effect. A variety of arrangements have been devised for turning this waste heat to account in raising steam for driving the machinery of iron works, and one of the simplest plans is to connect the working chambers of the puddling furnaces with a main flue for leading the gas under a steam boiler.

A still more effectual mode of utilising the waste heat of the gas from puddling furnaces is to transfer this surplus heat to the air used for supporting combustion, and, if the fuel is also used in a gaseous state, this plan of working can be still more advantageously practised. By this means the heat in the gas discharged from the puddling chamber is transferred to the combustible gas used as fuel, and to the air required for its combustion, so that as they both enter the working chamber at a very elevated temperature, the result produced by burning the gas is so much greater than it would be if the gas and air were at the normal atmospheric temperature, and a very considerable portion of the heat which would otherwise pass away and be wasted is turned to account. By thus gradually accumulating, within the working chamber, the heat passing off in the gaseous product of combustion, a very much higher temperature may be attained than is possible with ordinary furnaces.

The use of fuel in the form of combustible gas has long been practised in Germany and other parts of the continent where coal is scarce, and the materials used for the purpose have been either peat, as in Hanover, or wood and lignite, as in Carinthia and Styria, and it is only by such a contrivance that these inferior kinds of fuel could be made available for the puddling of iron and many other purposes. The use of gaseous fuel in this country has been adopted chiefly in connection with the above-mentioned regenerative system introduced by Mr. Siemens, and it has been applied not only in the furnaces used in glass making, etc., but also in puddling furnaces, reheating furnaces, etc. with very great advantage.

The composition of the gas produced from coal by burning it with an insufficient supply of air for converting the carbon into carbonic dioxide depends somewhat upon the kind of coal and the arrangement of the apparatus used, but the following analyses of the gas obtained at the St. Gobain glass works will serve to illustrate its general character:

		Volume	
Carbonic oxide	23·7	24·2	
Hydrogen	8·	8·2	34·6
Carburetted hydrogen	2·2	2·2	
Carbonic dioxide	4·1	—	
Nitrogen	61·5	4·2	
Oxygen	0·4	61·2	65·4
	99·9	100·	

The fuel used by Mr. Siemens for the production of combustible gas is coal of the kind that does not cake when heated. The gas producer employed for the purpose is represented in vertical section by fig. 409; it consists of a rectangular brick chamber having one of its sides (B) inclined at an angle of from 45° to 60°, and fitted with a grate (C) at the lower end. At the top the chamber has an opening (A) capable of being closed by a tight-fitting lid, and through this opening the coal in small fragments is supplied to the chamber so as to fall upon the inclined plane (B) and slide down until it forms a thick layer above the grate (C). By means of an arch above the inclined plane some of the coal is kept in the position shown in the drawing. Combustion takes place immediately above the grate (C), and carbonic oxide is produced either in consequence of the large excess of carbon presented to the air entering between the bars of the grate or by the action of the ignited coal upon any carbonic dioxide that may be formed. At the same time the coal overlying the ignited mass is subjected to destructive distillation, and thus the mixture of carbonic oxide and nitrogen passing up through it becomes mixed with hydrocarbon gases and vapours. The combustible gas thus produced passes out through the flue (H) at a rate regulated by the damper (D) and is then led through an underground conduit to the pipe (J) which is connected with the furnaces where the gas is to be burnt.

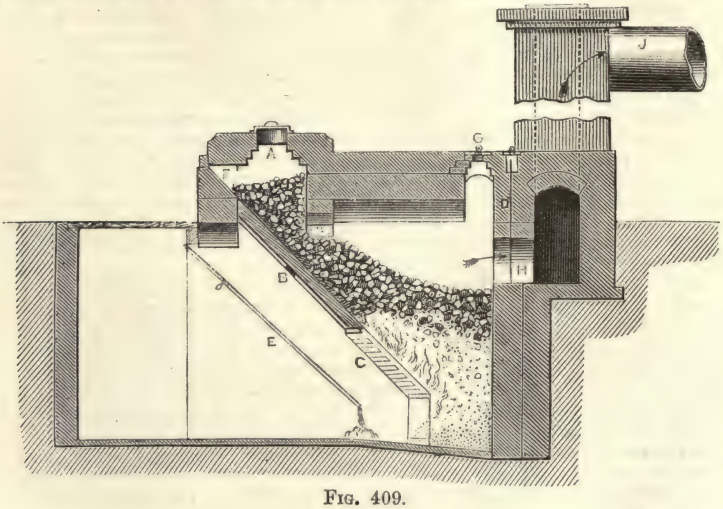


FIG. 409.

Siemens has applied the regenerative principle of economising heat to the construction of puddling furnaces, using gaseous fuel obtained by burning coal so as to produce carbonic oxide, and burning this in the puddling chamber. The general arrangement of this furnace is shown by figs 410, 411, and 412.

The bed of the puddling chamber (D D) is shown in section in fig. 411. It is formed of cast-iron plates, lined with a layer of ferric oxide and fitted with water bridges at the ends. Beneath the bed of the puddling chamber is a tank, into which the overflow from the water bridges escapes, and the evaporation from this tank keeps the iron plates of the bottom from becoming too hot. The steam passes away through the ventilating shafts (K K, fig. 412). On each side of the bed there are heating chambers (H H) in which the charge of pig iron is heated to redness before it is put into the puddling chamber.

The front elevation, fig. 410, shows the valve (B) through which the gas is passed into the flue (M) and then into the bottom of the chamber (C, fig. 411). Air is at the

same time passed into the chamber (E, fig. 411) through the flue (N, fig. 410). The gas and air, after passing through these chambers, rise through the flues (G G and F F F, fig.

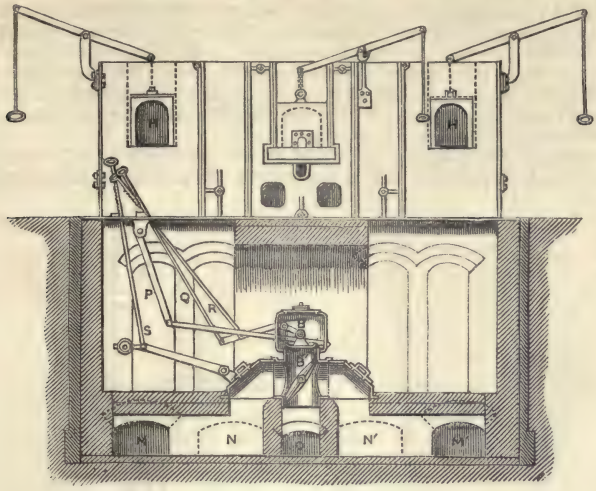


FIG. 410.

FIG. 411.

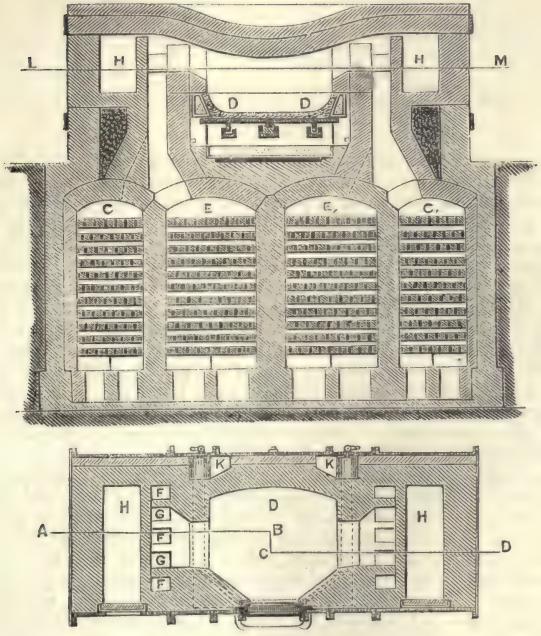


FIG. 412.

412) and combustion takes place when they meet in the puddling chamber. The product of combustion passes away through a corresponding series of flues at the opposite end of the furnace into the chambers (c' e') which become heated before the gas passes

away through the flues (M′ N′) into the chimney flue (O). When the furnace has worked for some time in this way, and the chambers (C′ E′) are sufficiently heated, the valve (B) is reversed by means of the lever (P), so that the currents of air and gas are made to pass through the chambers (C′ E′), where they become heated, and thus produce, on combustion, a proportionately higher temperature. The product of combustion then escapes through the flues (G F) and the chambers (M N) into the chimney flue (O). By thus alternately changing the direction of the currents of gas and air, the waste heat of the product of combustion is arrested in the brick chambers and transferred to the fresh supply of gas and air. The supply of gas and air in suitable proportions is regulated by valves worked by the levers (Q R S, fig. 410).

The necessity of keeping the pasty mass of iron constantly stirred while decarburation is effected by puddling, makes the work of the puddler so extremely laborious

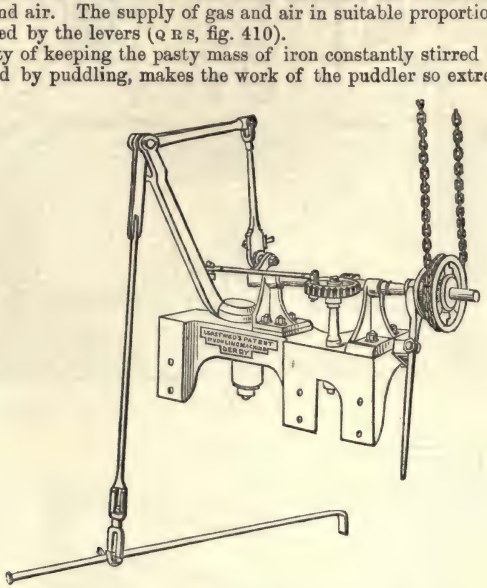


FIG. 413.

that various attempts have been made to carry out this part of the operation by machinery. It is, however, only within the last few years that any of these attempts have been successful in almost entirely doing away with the need for hand labour, at the same time shortening the operation, and economising the fuel as well as iron. The accompanying drawing, fig. 413, represents the arrangement of a mechanical puddler designed by Mr. Eastwood. It is fixed to the outside of the puddling furnace, and when the shaft is driven by the chain, the crank at its extremity raises the rabble by means of the bent lever and makes it move from back to front of the puddling chamber: at the same time the rabble is made to shift from side to side by the rod connecting the gib with the horizontal wheel driven by a worm pinion on the shaft. Every turn of the wheel alters the position of the gib upon which the rabble is supported, and thus the rabble is made to move over every part of the puddling bed. This arrangement is one of the simplest forms of mechanical stirrer, but it shares with others the disadvantage of being useless for balling the puddled iron, which is the most laborious part of the operation.

The idea of making the motion of the puddling chamber itself do the work of stirring the pasty iron has been practically carried out by Danks and Siemens with considerable success. The general arrangement of Danks' puddler is represented by figs. 414 and 415. The puddling chamber is cylindrical in shape and formed of cast-iron segments bolted together. Internally it is lined with fire brick and fettling, while on the outside there is a toothed wheel extending round the whole circumference of the iron casing. The chamber is supported on friction rollers, mounted on pillar blocks (B B), fixed to a bed plate (C, fig. 414), and is made to rotate by the pinion carried by the standard (A). Fig. 415 represents, on a smaller scale, a sectional elevation of the furnace (E, fig. 414)by which the puddling chamber (K) is heated, and the mode in which they are connected together by the flue (H). The ashpit of the furnace is closed and air is supplied partly by a fan through the pipe (G), partly also by the pipe (A), fitted with branches (C) by which the air is delivered in jets above the fuel burning upon the fire grate (F). The iron plate forming the fire bridge between

the back of the furnace and the puddling chamber has a coil of pipe cast in it through which water is made to circulate to keep it cool. At the opposite end of the

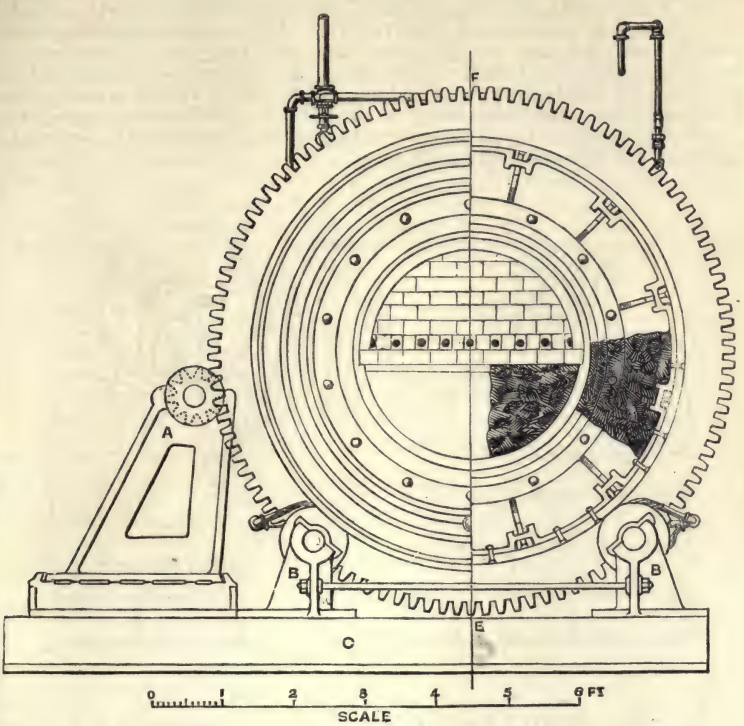


FIG. 414.

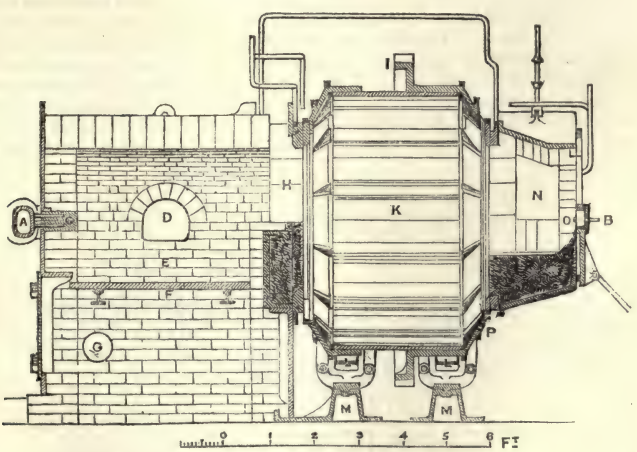


FIG. 415.

puddling chamber is a cover fitted in such a manner as to be moveable and to admit of the ball of malleable iron being taken out. At this end of the puddler there is a fixed flue by which it is connected with the chimney.

In working this puddler too much time would be lost by melting the pig iron in it; an ordinary cupola is used for the purpose, or the metal is run in directly from the smelting furnace.

The decarburised iron obtained by puddling is removed from the working chamber of the furnace in lumps termed puddle balls, which consist of intensely heated metallic iron in a spongy state, intermixed with melted slag and oxidised iron. In order to separate these admixtures and reduce the metallic iron to a compact and uniform mass, the puddle balls are either hammered or pressed while at a welding heat. This operation is termed blooming or shingling. The hammers employed for the purpose are termed forge hammers; they are very powerful and are constructed of cast iron, as represented by fig. 416.

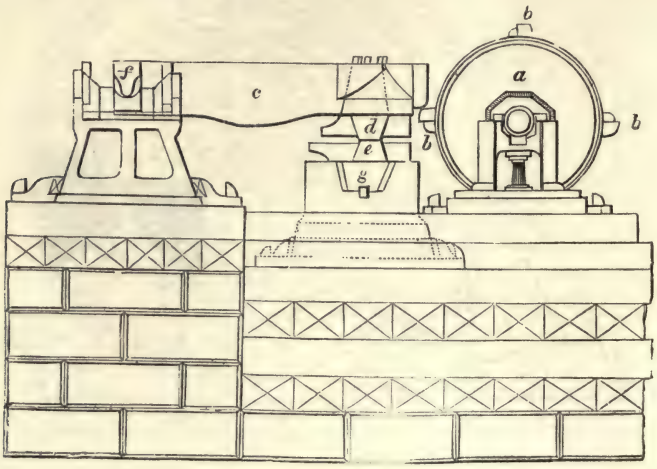


Fig. 416.

The massive beam (*c*) is 8 or 10 ft. long, and one end is supported on a fulcrum (*f*) upon which the beam is moveable, while the other end is fitted with a shaped head (*d*), and is lifted by the wipers (*b b b*) of the cam wheel (*a*), by the revolution of which the hammer head of the beam is made to fall at the rate of 70 or 80 strokes a minute upon the anvil (*e*) where the puddle ball is placed. A steam hammer is often used for this purpose, consisting of a block of iron weighing several tons, attached to the piston of a steam engine fixed above it, so that the block can be lifted vertically in guides fitted to the framework and let fall upon the puddle ball placed on an anvil.

The machines employed for compressing puddle balls are of various forms, and are termed squeezers. One of the most usual kinds represented by fig. 417 con-

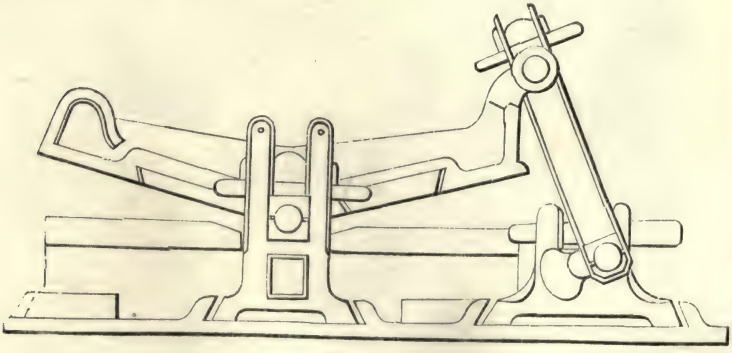


Fig. 417.

sists of a lever worked upon a fulcrum at the centre, by a crank connected to one end, so that the jaws are alternately brought at the rate of 60 or more strokes a minute nearer to the corresponding anvil faces of the stationary portion of the machine upon which the puddle balls are placed to receive the pressure.

Squeezers of this kind are now employed more generally than hammers for consolidating the puddle ball and converting it into a bloom. Sometimes the squeezer is of a different construction and consists of a strong cylindrical casting furnished at the inner surface with blunt triangular teeth, and within which a small rotating cylinder having similar teeth on the outer surface is fitted excentrically in such a manner that as it revolves the distance between the two cylinders gradually diminishes, and when the puddle ball is placed between them at the widest part it is gradually submitted to increasing pressure as it is carried forward by the rotating cylinder until it reaches the narrowest part, and is then ready for the rolling mill.

The puddle ball produced by Danks' rotatory puddler is very much larger than those produced by hand labour, and it often weighs five or six hundredweight. The ordinary form of squeezer is therefore insufficient for the purpose of working these large balls, and a specially constructed machine is necessary. It consists of two corrugated rollers (D D, fig. 418) about 4 feet long and 18 inches diameter, mounted side by side on axes turning in journals in the strong frame (B), and having at one end geared wheels, as shown in fig. 419, by which they can both be made to revolve in the same direction at the rate of fifteen or twenty revolutions per minute. Above these rollers, and mounted in the same frame, is a large excentric cam (A), which revolves in the same direction as the two rollers (D D). The periphery of this excentric revolves at the same rate as the circumference of the two rollers, and the puddle ball in passing between the excentric and the rollers is submitted to a gradually increasing pressure. In order to consolidate the mass of iron while passing between the rollers, there is fitted on one side of the squeezer a horizontal steam hammer, as shown in fig. 419, the ram (H) of which strikes the end of the ball as it is being squeezed. The head of this ram is seen at C, in fig. 418.

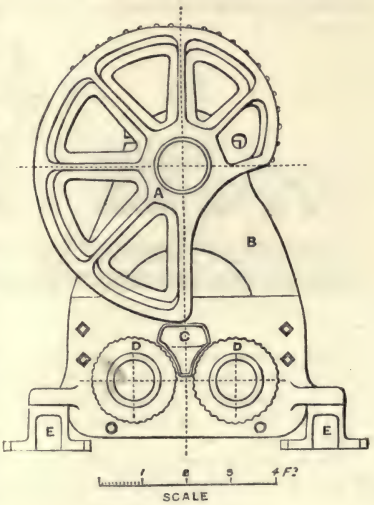


FIG. 418.

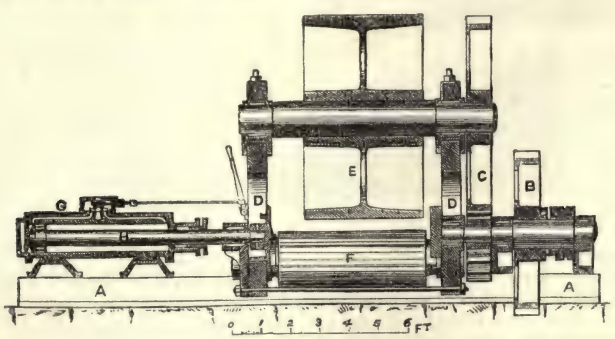


FIG. 419.

When the puddle ball has passed between the cam and rollers twice, it is removed and lifted by a crane to the reheating furnace before being taken to the rolls.

Hydraulic power is sometimes employed with advantage for compressing and consolidating large masses of decarburised iron, since intense pressure can be produced

without concussion, and the massive foundations requisite for steam hammers can be dispensed with. An hydraulic machine of this kind constructed by Haswell of Vienna consists of a long vertical hydraulic press the ram of which acts downwards against a table serving as an anvil. This ram is lifted by a smaller hydraulic press with which it is connected, and as the ram rises the water expelled from the larger cylinder is returned to an accumulator containing a piston, upon the surface of which steam can be admitted when it is desired to move the ram rapidly. When the full power of the machine is required, the connection between the press and the accumulator is cut off, and the press is connected with a pair of hydraulic pumps driven by a direct-acting steam engine.

The hammering or squeezing of the puddle balls occupies only a few seconds, and when it has been somewhat consolidated in this way, it is termed a bloom; it is then rapidly passed several times between grooved rollers while still red hot and is thus drawn out into a bar. The rollers used for this purpose, constituting what is termed a forge train, consist of two pairs of rollers (R F) fitted in frames and driven by machinery. The pair of rollers (R), called roughing rolls, have corresponding V-shaped grooves round the surfaces. The other pair of rollers, termed finishing rolls,

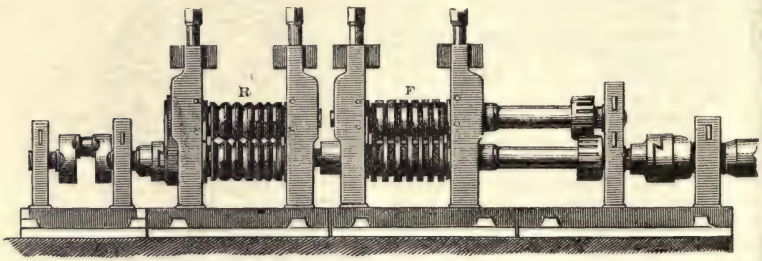


FIG. 420.

have flat grooves, and in both cases the grooves gradually decrease in size from one end of the roller to the other, so that by passing the blooms successively through several pairs of grooves they are reduced to bars, measuring from 7 to 3 inches in width, by from $1\frac{1}{2}$ to $\frac{1}{2}$ an inch in thickness. In this condition the iron is termed puddle bars or No. 1 iron.

The iron after leaving the rolls in the state of puddle bars, and while still hot, is cut up into short lengths, by means of powerful shears, and the pieces are tied together with strong wire in bundles termed piles, which are then brought to a welding heat in a reverberatory furnace, called the reheating furnace or mill furnace, constructed somewhat like a puddling furnace, as shown in fig. 421, in vertical section. The hearth (*a*) of this furnace on which the iron piles are placed is made of sand and it slopes down towards the chimney flue, so that any slag that is formed may run down and escape through the hole (*b*), leaving the hearth quite dry.

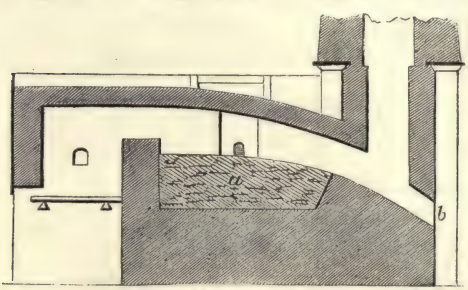


FIG. 421.

The piles are raised as rapidly as possible to a full welding heat in the mill furnace, and are then removed from the hearth with tongs to mill rolls of a similar kind to those already described, but more highly finished, and they are again drawn out into bars, which are a second time cut into short lengths, piled and submitted to the same operations of heating and rolling several times according to the required quality of the iron. After the first rolling of the iron into puddle bars, hammering is sometimes substituted in the place of drawing out between rollers. It is in this series of operations that the iron acquires texture, and that close uniform and continuous fibre upon which the strength and general good quality of malleable iron is considered to be chiefly dependent. The mode in which the pieces of iron are arranged in the piles is considered to be of great importance as regards the result obtained.

During the reheating of the piles in the mill furnace a certain proportion of slag is produced which has a composition very similar to that of the slag from the puddling furnace; but the silica it contains is mainly derived from the sand forming the hearth of the furnace.

Analyses of Mill-furnace Slag.

	Dowlais	Wasseralfingen	Sweden	—
	Riley	Rammelsberg	Dugent	Noad
Ferric oxide	—	8·49	—	5·00
Ferrous oxide	66·01	55·36	65·83	52·50
Manganous oxide	0·19	—	0·74	—
Alumina	2·47	—	—	9·60
Lime	0·81	0·36	—	—
Magnesia	0·27	trace	—	—
Silica	28·71	34·00	33·47	32·00
Sulphur	0·11	—	—	—
Ferrous sulphide	—	—	—	1·95
Phosphoric acid	1·22	—	—	0·25
Copper	trace	—	—	—
	99·79	98·21	100·04	101·30
Percentage of iron	51·34	49·0	51·20	45·34

When all these successive operations have been completed, the iron is in the condition known as **merchant iron**, and the different degrees of quality are indicated as No. 2, No. 3, etc., or as 'common,' 'best,' and 'best best,' as well as by particular brands.

Besides the waste of iron resulting from the formation of slag in refining, puddling, etc., there is always a further waste due to the oxidation of hot iron while passing through the operations of shingling, hammering, and rolling to which it is subjected. The product of this oxidation consists chiefly of magnetic oxide, which forms a crust on the surface of the hot iron and falls off in scales, constituting what is known as **hammer scale** or **mill scale**.

The total waste of iron in the conversion of pig iron into malleable iron varies according to the kind of pig iron operated upon, and the amount of impurities to be got rid of; to some extent also it depends upon the skill of the workmen. The greater part of the waste of iron takes place in the refining, and on the average it amounts to about 10 per cent. of the pig iron. In puddling refined iron the waste does not amount to more than from 4 to 7 per cent. In the mill furnace the waste is much less, varying from 5 to 6 per cent. according to the number of times the piles are reheated, and the size to which the iron is rolled.

The consumption of fuel in the various stages of the conversion of pig iron into malleable iron varies according to the skill of the workmen, as well as the kind of fuel and pig iron used.

In refining from 6½ to 8 cwt. of coke is used for each ton of metal produced when the pig iron has to be melted, and when the charge is run into the refinery direct from the smelting furnace from 4 to 5 cwt of coke per ton of metal is sufficient.

In pig boiling the consumption of coal varies from 18 to 22 cwt. per ton of bar iron made, according as the coal is more or less bituminous and capable of burning with flame.

In puddling refined metal the consumption of fuel is about 10 or 14 cwt.. of bituminous coal, and from 17 to 18 cwt. of anthracitic coal, per ton of iron made.

In heating the piles the consumption of fuel ranges from 7 cwt to 13 cwt. per ton of merchant bars, according as they are large or small.

Ordinary malleable iron has a grey colour, which varies in its shade according to the character of the iron, and has sometimes a bluish or blackish tinge. The specific gravity ranges between 7·3 and 7·9, that of the better kinds approximating to the mean of these two limits. The specific gravity is to some extent affected by the alteration of mechanical texture produced mechanically. Thus a bar, 4 inches wide and 1 inch thick, having a specific gravity of 7·801, acquired a specific gravity of 7·8621 when rolled out to a very thin sheet, and iron of 7·7938 specific gravity acquired a specific gravity of 7·8425 when drawn into very thin wire

The specific heat of ordinary malleable iron is 0·113795; it is somewhat higher when the amount of carbon in the metal is large. The conductivity for heat is 374·3 as compared with gold = 1000. The linear and cubic expansion by heat is less than that of most other metals. The linear expansion for each degree between 100° and 300° is $\frac{1}{85\frac{1}{100}}$. An iron bar expands $\frac{3}{560}$ when raised from a red heat to a white heat, and $\frac{7}{560}$ when heated from 20° to whiteness.

The melting point of malleable iron has not been determined with any degree of accuracy. It is between the melting point of cast iron and that of platinum; it is estimated at 1550° by Pouillet, and at 2000° by Scheerer, and there is no doubt it is higher in proportion as the metal contains less carbon.

Pure iron is attracted by the magnet more powerfully than iron containing carbon; but it does not retain the magnetic condition so long as the iron containing some carbon. Ordinary malleable iron is also more strongly attracted than steel, and it is more easily rendered magnetic, but it loses the polar condition much sooner than steel does. It appears, therefore, that the presence of a certain amount of carbon is in some way necessary for the retention of the magnetic condition by iron. Bars of iron placed vertically, or nearly so, become, in course of time, magnetic. The magnetic condition of iron is very nearly destroyed by a red heat, and entirely so by exposure to a white heat.

The electric conductivity of malleable iron is much less than that of copper. Taking this as 100, that of iron is 20 according to Harris, 17·74 according to Lenz, and 15·8 according to Becquerel. Matthiessen considered the conductivity of pure electro-deposited iron to be much higher than that of ordinary malleable iron.

The hardness of malleable iron varies considerably; it is influenced by the presence of foreign substances and reduced by increase of temperature. It is but very slightly increased by sudden cooling of the red-hot metal, and less so in proportion as the amount of carbon in the metal is smaller. The hardness of malleable iron seems to be essentially dependent upon the presence of a certain amount of carbon in the metal. Absolutely pure iron is so soft that it offers but little resistance to friction.

The tenacity of malleable iron also varies very much, and is influenced by the nature of the foreign admixtures in the metal, by their amount, and by the internal texture of the metal, by temperature, and other conditions. Up to a temperature of 146° the tenacity of boiler plate is not sensibly diminished; but at a red heat it is reduced one-fourth. According to Fairbairn, the tenacity of good rivet iron at 190° is one-third greater than at the ordinary temperature, but at a red heat it is reduced to nearly one-half.

Tenacity or Tensile Strength of Malleable Iron.

Kind of iron	Lengthwise in pounds per square inch	Crosswise in pounds per square inch	Ultimate extension	Authority.
Lowmore iron wire . .	64,200	52,490	—	Fairbairn
Staffordshire bar iron .	from 62,231 to 56,715		·302 ·186	Kerkaldy and Napier.
Swedish bar iron . .	from 48,232 to 47,855		·264 ·278	

The malleability of iron containing from 0·25 to 0·5 per cent. of carbon is very considerable, though less than that of silver or gold. It is influenced by the presence of the foreign substances which modify the hardness and tenacity of the metal; the degree of malleability being apparently determined chiefly by the relative hardness and tenacity, but to some extent also by the internal texture, of the metal. The malleability of iron is increased in proportion as the temperature is raised, and iron becomes very much softer without its tenacity being proportionately lessened. At a red heat the metal is sufficiently soft to be brought into any required shape by hammering or rolling, and at a white heat it becomes quite pasty, so that separate pieces may be, as it were, kneaded together into one mass, or, as it is termed, w e l d e d. This capability of being forged and welded, so important as regards the working of iron for various useful purposes, is partly referable to the wide interval between the temperature at which the metal presents its ordinary degree of hardness, and that at which it becomes liquid: partly, also, to the fact that at temperatures far below the melting point iron acquires a soft plastic condition which is retained in some degree through a considerable range of temperature.

Among the foreign substances influencing prejudicially the malleability of iron, the chief are sulphur, phosphorus, and silicon. The first communicates to iron the character of being brittle while hot, or, as it is called, r e d s h o r t in forging. Phosphorus

renders malleable iron cold short, or brittle and weak, at the ordinary temperature. Silicon has a similar influence in a higher degree. Manganese seems to be beneficial rather than otherwise as regards the malleability of iron. When red-hot iron is immersed in cold water the malleability is considerably reduced. The same effect is produced by long hammering or rolling, but the malleability is again restored by heating the metal to redness and allowing it to cool gradually.

The texture or molecular structure of iron varies considerably according to the treatment the metal has been subjected to. After fusion, iron is decidedly crystalline or granular, and the fractured surface presents distinct indications of that condition. By hammering or rolling the metal while hot, it acquires a fibrous texture, becomes more tenacious, less susceptible of true fracture, and capable only of being torn asunder. In the usual method of producing malleable iron the metal is not melted but wrought mechanically while in a kind of doughy condition, and the uniform close fibrous texture which determines the quality of the metal depends very much upon the nature of this treatment and the extent to which it is carried.

By hammering fibrous iron while cold it is rendered harder and brittle; when afterwards broken the metal presents a granular or crystalline fracture, but opinions differ as to whether this crystalline condition is really a result of the hammering. This is also the case in regard to the influence of long-continued pressure, vibration, or concussive action, etc. in affecting the texture of malleable iron, some maintaining that under these conditions the fibrous texture of the metal is gradually destroyed, and its strength reduced.

Malleable iron undergoes no change in dry air, or in water free from air; but in moist air, or in water containing air, it gradually becomes oxidised or rusted at the surface, and, after exposure for a sufficient length of time, the entire mass may be eventually converted into oxide. The carbonic acid present in atmospheric air appears to contribute largely to the production of this change. The presence of saline substances in water also facilitates the oxidation of iron, while alkalies and oily or resinous substances retard the oxidation. Contact with more highly electro-positive metals, such as zinc, also hinders the oxidation of iron within a certain distance around the point of contact.

At a temperature of about 230°, iron becomes capable of combining directly with atmospheric oxygen, and the polished surface of the metal at first becomes covered with an extremely thin film of magnetic oxide, presenting a yellow colour which gradually passes into a red, blue, and grey. At a red heat this film of oxide becomes thicker and forms a crust, which separates as the metal cools, constituting what is commonly known as forge scale, and when the iron is kept hot for some considerable time the outer surface of the crust is converted, by further oxidation, into ferric oxide. At a white heat iron burns in the air with production of magnetic oxide, and this combustion may be sustained for some time by directing a blast of air upon the heated metal.

At a temperature of about 390°, malleable iron decomposes water vapour, forming magnetic oxide and liberating hydrogen. It is dissolved completely by strong hydrochloric acid; but with dilute acid a carbonaceous residue is left undissolved. In both cases the hydrogen evolved carries with it a carburetted vapour or gas which communicates to the hydrogen a peculiar smell.

Malleable iron generally contains from 0·25 to 0·5 per cent. of carbon, but sometimes the amount of carbon is much less, and in a few instances it is higher. The smaller the amount of carbon, the softer is the iron, and the larger the amount of carbon within these limits, the nearer does the metal approximate to the character of steel. The only ordinary iron that is probably quite free from carbon is that technically known as burnt iron, which cannot be soundly welded. Hence it has been supposed that the capability of being welded is determined by the presence of some carbon in the metal. It is more probable, however, that the peculiarity of burnt iron in this respect is only indirectly determined by the absence of carbon, and that it is due to the presence of a minute quantity of oxide in the metal, which could not have been introduced so long as any carbon remained in it.

Among the foreign substances other than carbon, which are often present in malleable iron, the most important are sulphur, phosphorus, and silicon, existing probably in combination with equivalent proportions of the metal as sulphide, phosphide and silicide.

Sulphur is generally present to some extent in most kinds of malleable iron, and even when amounting to only 0·034 per cent. it has the effect of rendering the metal red short, and liable to crack at the edges in forging. It has been considered that 0·01 per cent. of sulphur is the highest amount consistent with the usefulness of malleable iron.

Phosphorus is also frequently present, and when amounting to 0·75 per cent. it

renders the metal very weak and brittle at the ordinary temperature, or, as it is called, cold short. In smaller amounts it is, however, considered to be serviceable in rendering the metal more capable of being welded.

Silicon renders malleable iron harder and lessens its tenacity, making it what is termed rotten in working, even when present only to the extent of 0·37 per cent.

Manganese is considered to render malleable iron harder, but not to make it steely.

Copper is considered to render malleable iron red short, and to reduce the capability of being welded, without, however, affecting the tenacity of the metal.

The following table gives the composition of several kinds of malleable iron which illustrate the extent to which the above-mentioned substances are present.

Kind of iron	Fe	C	Si	S	P	Mn	As	Analyst
Swedish . .	99·863	·054	·028	·055	trace	trace	—	Henry
,, . .	99·22	·087	·056	·063	·005	—	trace	,,
,, . .	99·544	·087	·115	·220	·034	—	trace	,,
,, . .	99·73	·24	·03	—	trace	trace	—	Karsten
Silesian . .	99·873	·09	·03	·007	—	—	—	,,
Russian . .	99·412	·272	·062	·234	—	·02	trace	Henry
,, . .	99·594	·34	trace	·066	—	trace	—	,,
Welsh . .	97·72	—	·26	·21	·71	—	—	Riley
,, . .	98·54	—	·13	·05	·42	—	—	,,
Shropshire . .	—	—	·18	·06	·37	—	—	Price
,, . .	—	—	·18	·03	·30	—	—	,,
Lowmoor . .	99·372	·016	·122	·104	·106	·28	—	Tookey
Weardale . .	—	·17	·11	·058	·089	·33	—	Percy
Russell's Hall .	99·361	·19	·144	·165	·14	—	—	Henry

Manufacture of Steel.—By smelting very rich iron with charcoal in a bloomery much in the same way that malleable iron is produced directly (see p. 579) the metal may be obtained in the state of *steel*, and possessing the character of acquiring considerable hardness when suddenly cooled. This method of manufacture was formerly much practised; but it is now almost entirely superseded and steel is generally produced either by the carburation of malleable iron or by the decarburation of pig iron. The steel made by the former method is termed cement steel and that made by decarburising pig iron in a charcoal finery is termed natural steel. Pig iron is also converted into steel by puddling and by the action of atmospheric oxygen on the melted metal according to the method of Bessemer.

In addition to these indirect methods of manufacture, attempts have lately been made to produce steel directly from iron ore by methods more easily manageable than smelting in the bloomery; among these the application of the regenerative furnace by Siemens is most worthy of consideration. The arrangement adopted is shown by fig. 422. The furnace is similar in construction to the gas puddling furnace already described, but above the combustion chamber (F F) there are two cylindrical hoppers (A A) formed of cast iron, in which the iron ore is subjected to the action of reducing gas, which is passed into the hoppers through wrought-iron pipes (G G) connected with the supply main (B). The lower extremities of these hoppers projecting into the combustion chamber (F F) are made of fire clay in order to resist the high temperature. The upper part of each hopper is surrounded by a flue (S S S S) into which the flame from the furnace ascends and keeps the contents of the hoppers at a proper temperature.

In starting the operation in this furnace some pig iron is placed on the hearth, together with sufficient charcoal to support the iron ore in the hoppers (A A). The gas is then turned on and ignited in the usual way, and by the time the pig iron has melted, the ore in the lower ends of the coppers will have been reduced to a metallic sponge, which sinks down and is gradually dissolved in the melted pig iron, while fresh portions of the ore are reduced in the same way. This is continued until the amount of carbon in the liquid metal upon the hearth corresponds with the kind of steel required and then the charge is run off into ingot moulds.

Since the reduction of the iron ore in this way takes place but slowly, this part of the operation has since been carried out in a rotatory chamber, consisting of a cylindrical iron tube lined with fire brick. This chamber is mounted on friction rollers and fitted with a toothed wheel by which it is made to revolve slowly while the contents are subjected to the action of heat produced by the combustion of gas supplied together with air at a high temperature from a series of regenerators.

In carrying out the manufacture of steel by this method, an unanticipated difficulty was encountered in the absorption of sulphur by the spongy metal, and consequently recourse was had to the plan of melting the iron ore with fluxes and then precipitating the iron from the liquid mass by mixing it with carbon in the form of coal.

For this purpose the ore is mixed with sufficient lime to prevent the combination of much ferrous oxide with the silica present, and a charge of about a ton is put into

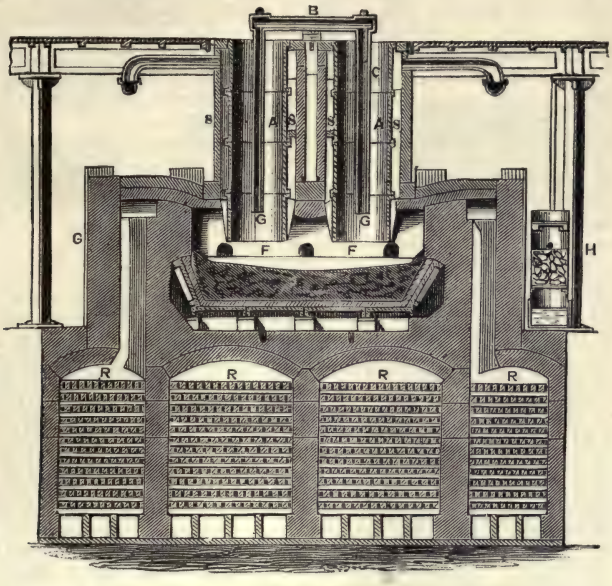


Fig. 422.

the rotating furnace previously heated to bright redness. Sometimes aluminous iron ore is added when the iron ore contains much silica, and the addition of materials containing manganese is also advantageous. After the cylinder has been made to revolve slowly for about 40 minutes and, under the influence of the flame, the contents have acquired a bright red heat, about 5 or 6 cwts. of small coal is added, and the cylinder made to rotate more rapidly to effect a thorough intermixture. By the reaction of the carbon and ferric oxide, magnetic oxide is first formed, which melts, and at the same time metallic iron begins to be deposited, while the remaining ingredients of the iron ore and the flux form a silicious slag. During the continuance of this reaction carbonic oxide is evolved in such abundance that the supply of gas to the cylinder can be almost entirely shut off, and only air requires to be supplied to burn the carbonic oxide evolved by the reaction.

When the reduction of the iron ore is nearly completed, the rotation of the cylinder is stopped and the liquid slag is drawn off. Then by rotating the cylinder again the loose lumps of metal are united into balls, which are transferred to a steel melting furnace containing some melted pig iron where they are run down, and the resulting melted steel is then cast into ingots.

Carburation method : cementation.—This method of producing steel is based upon the circumstance that when malleable iron is heated to a temperature somewhat below its melting point, in contact with charcoal or some other carbonaceous substance and without access of air, carbon is absorbed by the metal.

The malleable iron used for producing steel in this way must be of the best quality and free from the impurities which affect the character of steel. The carburising material or cement used in the operation is coarsely powdered charcoal, and sometimes this is mixed with horn shavings, ferrocyanides, and similar substances containing carbon.

The furnaces in which the operation is conducted somewhat resemble glass-house furnaces in their general arrangement, as shown by figs. 423 and 424. They are constructed so that a uniform temperature may be kept up in them for several

days, the hot air from the furnace (A B) passing through the horizontal and vertical flues *d d* round the chambers (C C), which are constructed of fire bricks and serve to

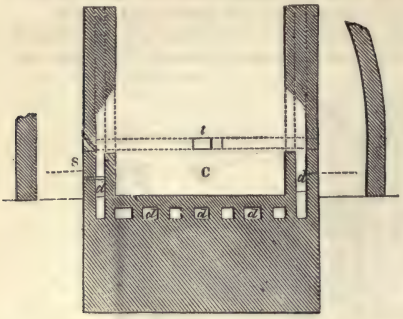


FIG. 423.

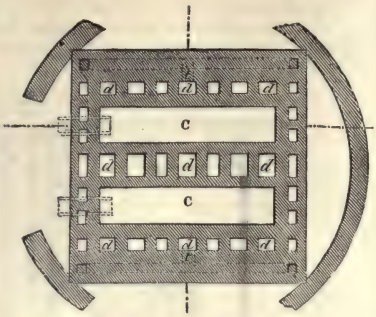


FIG. 424.

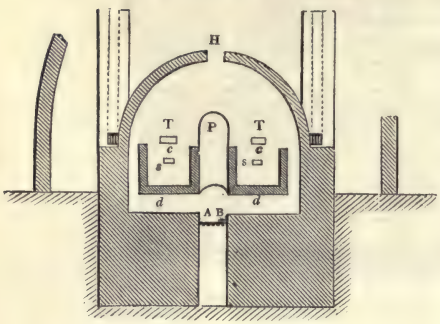


FIG. 425.

receive the bars of iron which are to be converted into steel. In charging these chambers or pots the bars of iron are imbedded in finely ground charcoal, and when the chambers are filled the surfaces are covered with a layer of loam. The doorway (P) is then bricked up, and the furnace is gradually heated up to the requisite temperature, which is kept up uniformly for several days until the conversion of the iron into steel is complete. The precise nature of the process by which iron is thus converted into steel is not thoroughly understood; but it is probable that gaseous carbon compounds, such as carbonic oxide or hydrocarbons, are concerned in the change, either by a reaction similar to that which takes place in the production of pig iron, or by the absorption of carbon from hydrocarbons, which takes place when malleable iron is heated in contact with marsh gas or olefiant gas.

When the conversion of the iron into steel is complete, the furnace is allowed to cool gradually and the bars are taken out. A remarkable characteristic of the steel produced in this way is the presence of numerous small blisters on the surface of the bars, for which reason it is called blister steel. The uniform size and distribution of the blisters over the surfaces of the bars are considered to indicate the good quality of the steel, while, on the contrary, if the blisters are large and unequally distributed the steel is probably deficient in homogeneity.

Iron, when converted into steel by the cementation method, increases in weight from 0·5 to 0·75 per cent., and the fuel consumed in the operation amounts to 75 or 90 per cent. of the steel produced.

The bars of blister steel obtained by the cementation method are never uniform throughout in texture and composition, the exterior portions being more highly carburised than the interior, and the difference is not always the same in all parts of the bars. To render steel made in this way homogeneous, the bars are heated and drawn out while hot under hammers into thin bars, which are laid together in a faggot, heated to a welding heat, and then hammered or rolled so as to weld them together into one mass. This operation is repeated several times, until the metal has acquired the requisite degree of homogeneity, and the steel is then termed shear steel.

The physical characters of the metal are also considerably changed during the cementation, and the surfaces of fracture present a crystalline or granular texture very different from that of malleable iron; the colour also is reddish white, somewhat like bismuth.

Another method of producing steel by carburetting malleable iron consists in melting scrap iron with sufficient pig iron to furnish the requisite amount of carbon.

The practical success of this method is principally due to the application of furnaces in which gaseous fuel is burnt upon the regenerative system introduced by Mr. Siemens. The furnace employed for the purpose is similar to that represented by fig. 410, the beds upon which the pig iron is melted being formed of refractory sand, and at the side o. it is an ordinary reverberatory furnace in which the malleable iron is heated to redness before being added to the bath of liquid pig iron in which it is dissolved, until metal of the required character has been produced. A prominent advantage of this method is that of obtaining considerable masses of steel in a liquid state, which facilitates the production of homogeneous steel.

Decarburation methods.—The production of steel from pig iron by abstracting a portion of its carbon is in all cases effected chiefly by means of the oxidising action of atmospheric oxygen, and to some extent also by reaction with slag containing ferrous silicate, much the same as in the production of ordinary malleable iron; but the nature of the metal produced is very much determined by the extent to which the decarburation is carried.

When the operation is conducted in a finery hearth with charcoal, the metal produced is termed *natural steel*. The material operated upon is either white pig iron or easily fusible grey pig iron obtained by smelting spathic or magnetic iron ore with charcoal. The decarburising operation was formerly conducted in this manner with a great variety of modifications in minor details, determined chiefly by the particular nature of the pig iron to be worked or by other local circumstances. In Westphalia, Silesia, Styria, Carinthia, Sweden, and some other places, steel was largely produced in this way, but of late years other methods have been to a great extent substituted for the decarburation in the finery hearth.

Among the more recent methods of producing steel, that of puddling is conducted essentially in the same manner as in the production of ordinary malleable iron, except in so far that the decarburation is not carried to the same extent, and the pig iron operated upon requires to be free from substances prejudicial to steel.

The greatest advance in the manufacture of steel has been effected by the introduction of Bessemer's method of decarburising pig iron, by blowing atmospheric air into the melted metal. Under these conditions the carbon is oxidised more readily than the iron, and converted into carbonic oxide with considerable evolution of heat, so that the temperature of the metal is kept above the melting point of steel, and when the decarburation has been carried far enough, the liquid steel can be run into moulds.

The apparatus employed in Sweden in the production of steel according to Bessemer's method consists of an upright cylindrical chamber constructed of fire brick strongly cased with sheet iron. At one side of the chamber is an opening through which melted pig iron can be run in, and the top is closed by a moveable cover of similar construction, having an open neck through which the gas evolved during the operation can escape. At the bottom of the chamber is a tapping hole that can be closed with a plug, and a gutter for running out the decarburised metal. Round the bottom also are a number of concentric tuyeres connected with a main through which air can be forced through the contents of the chamber. The melted pig iron is either run into the converting chamber direct from the smelting furnace where it is made, or it is first run into a large ladle and weighed. This plan has the advantage of saving the fuel requisite for melting the pig iron, and it is well suited for cases where the ore smelted yields pure pig iron of uniform quality.

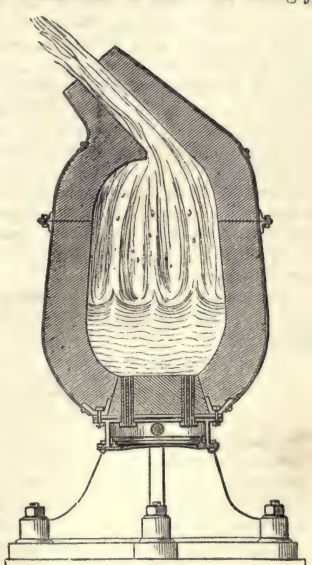


Fig. 426.

The converter used in this country is represented by fig. 426: it is an egg-shaped vessel made of stout sheet iron, and lined with fire brick or some other refractory silicious material.

At the bottom of the converter are a number of air tuyeres communicating with a lateral tube, by which air can be forced into the interior under a high pressure, and the upper end of the converter is furnished with a contracted neck, which is left open. The converter is mounted upon trunnions in such a manner that it can be turned over into any required position

by means of machinery connected with it. The general arrangement of these vessels in pairs is shown by fig. 427.

The converters (A A) are placed on opposite sides of a deep cylindrical pit, in the centre of which is a water-pressure engine with a vertical cylinder and a solid piston (G), having at the upper end a strong crosshead (D), formed of two strong parallel girders braced together, and arranged in such a manner as to hold at one end the ladle (C), while at the other end there is a counterpoise weight (E) which can be shifted to and from the centre of the crosshead according as the ladle (C) is full or empty. The ladle can be moved round the circumference of the pit opposite to either of the converters to be filled, or over any of the ingot moulds which are placed round the periphery of the pit. For this purpose the crosshead is raised up by the water-pressure engine at the centre of the pit, sufficiently high to clear the moulds; and by means of a hole at the bottom of the ladle fitted with a plug, the contents can be run into the ingot moulds in succession. The hydraulic engines (*l n*) are used for tipping the converters to discharge their contents into the ladle.

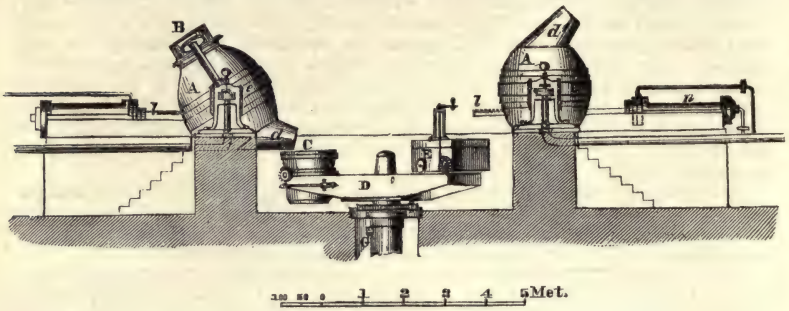


FIG. 427.

In working this apparatus, the charge of pig iron, varying from one and a half to five tons, is first melted in a cupola or reverberatory furnace, and run into the converter, previously heated to redness by burning a quantity of coke inside it. While the melted pig iron is being run in, the converter is placed so that the bottom and the neck are level with the central axis, and while it is being brought back to the vertical position the blast is turned on. A reddish-yellow faintly luminous flame then issues from the neck of the converter for a few minutes; after a while it becomes more brilliant, the liquid metal becomes violently agitated, and a shower of sparks appears, consisting of fragments of burning iron together with particles of slag, which are thrown out by the rapid disengagement of carbonic oxide. After some minutes the discharge of sparks ceases, the action becomes less violent, and the flame presents the bluish violet characteristic of carbonic oxide, until, when the whole of the carbon is oxidised, it is replaced by a stream of intensely heated gas, consisting chiefly of nitrogen resulting from the oxidation of iron by the air. At this period the converter is turned round to the horizontal position, and about 10 per cent. of manganiferous pig iron is run in or a sufficient quantity to give the requisite amount of carbon in the metal. The contents of the converter are then run out into a ladle and transferred to ingot moulds.

The chemical changes that take place in the converter are indicated by the following table showing the composition of the gas evolved at different stages of the Bessemer operation:—

	Two minutes	Four minutes	Six minutes	Ten minutes	Twelve minutes	Fourteen minutes
Carbonic oxide . .	—	3·95	4·52	19·59	29·30	31·11
Carbonic dioxide . .	10·71	8·57	8·20	3·58	2·30	1·34
Oxygen . . .	·92	—	—	—	—	—
Hydrogen . . .	8 8·37	·88	2·00	2·00	2·16	2·00
Nitrogen . . .		86·58	85·28	74·83	66·24	65·55

The corresponding alteration in the composition of the metal is shown by the following analyses by Snelus of portions taken out of the converter during the different stages of the operation:—

	Grey pig operated upon	Composition of metal after blowing			Steel	
		Six minutes	Nine minutes	Thirteen minutes	Ingot	Rail
Carbon { graphitic	2·070	—	—	—	—	—
Carbon { combined	1·200	2·170	1·550	·097	·566	·519
Silicon	1·952	·795	·635	·020	·030	·030
Sulphur	·014	trace	trace	trace	trace	trace
Phosphorus	·048	·051	·064	·067	·053	·053
Manganese	·086	trace	trace	trace	·309	·309
Copper	—	—	—	—	·039	·039

It will be seen that the sulphur present in the pig iron is almost entirely eliminated; the greater part of the silicon is also separated, together with the carbon, and almost in the same proportion; but the phosphorus is not removed, and, owing to the oxidation of some iron, the amount is actually greater in the finished steel than in the pig iron. The copper and manganese present in the steel are due to the manganiferous pig iron added at the end of the operation. The following analyses of the metal in different stages represent the results obtained at the Neuberg works in Styria, which are essentially of the same nature as those obtained at Dowlais. The copper and manganese in this case are chiefly derived from the pig iron operated upon, and the copper is due to the presence of pyrites in the spathic iron ore from which the pig is made.

	Grey pig operated upon	Composition of metal			
		After scorification	Towards end of boiling	Before adding manganiferous pig iron	Ingot
Carbon { graphitic	3·180	—	—	—	—
Carbon { combined	·750	2·465	·949	·087	·234
Silicon	1·960	·443	·112	·028	·033
Sulphur	·018	trace	trace	trace	trace
Phosphorus	·040	·040	·045	·045	·044
Manganese	3·460	1·645	·429	·113	·139
Copper	·085	·091	·095	·120	·105

The composition of the slag taken from the converter at the same time as the different portions of iron is shown in the following table:—

	Smelting furnace slag	After scorification	Towards end of boiling	Before adding pig iron	While casting
Ferrous oxide	0·60	6·78	5·50	16·86	15·43
Manganous oxide	2·18	37·00	37·90	32·23	31·89
Lime	30·35	2·98	1·76	1·19	1·23
Magnesia	16·32	1·53	0·45	·52	·61
Potash	·18	trace	—	—	—
Soda	·14	—	—	—	—
Silica	40·95	46·78	51·75	46·75	47·25
Alumina	8·70	4·65	2·98	2·80	3·45
Sulphur	·34	·04	trace	trace	trace
Phosphorus	·01	·03	·02	·01	·01
	99·77	99·79	100·36	100·36	99·87

It is evident from these analyses and from those showing the composition of the metal and of the gas given off, that the heat generated in the decarburation of pig iron by the Bessemer method is in great measure due to the oxidation of silicon, since the carbon is chiefly separated as carbonic oxide, and consequently it appears that the pig iron to be converted into steel by that method should contain a considerable amount of silicon; at the same time the amount of silicon should not exceed the quantity capable of being oxidised by the time the carbon is burnt off and the end of

the operation is indicated by the cessation of the flame, otherwise the steel produced may retain sufficient silicon to render it weak and brittle, or the excess of silicon will give rise to the formation of a large amount of slag, and consequent waste of iron by oxidation and the production of ferrous silicate. The oxidation of iron or manganese in the formation of slag is also a further source of heat.

The uniformity of composition and texture essential to steel of good quality may be to a great extent ensured by subjecting blistered steel or puddled steel to repeated welding and forging or rolling. But this method is laborious, while it has the further disadvantage that in carrying it out the amount of carbon in the metal is reduced by oxidation and the metal is thus rendered softer. By melting the steel in crucibles, however, it is possible to exclude air, and thus to obtain under the name of cast steel a more perfectly homogeneous metal. This method of treating cement steel has been practised since 1740, when it was introduced by Huntsman at Handsworth, near Sheffield. The more recent methods of Bessemer and Siemens have furnished steel in a melted condition, and have thus to some extent superseded the necessity for subjecting cement steel, etc., to this operation, but it is still practised on a considerable scale.

The material used for the production of cast steel of high quality, whether it be cement steel or puddled steel, must be free from impurities, and, according to the amount of carbon in the metal operated upon, as well as the kind of steel required, various substances are used as admixtures—such as charcoal, manganese, and manganiferous pig iron.

The metal is melted in crucibles so as to exclude access of air, and as it is important that the fusion should take place rapidly, Siemens' regenerative furnaces have been employed for this purpose with great advantage. The melted metal is run into ingots, which are generally of unequal texture, and to render them compact and uniform, they are heated and drawn out under powerful hammers until the metal acquires the requisite characters.

The characters of steel are to some extent intermediate between those of cast iron and ordinary malleable iron, but steel is distinguished from both by the capability of acquiring considerable hardness when suddenly cooled. The greater the reduction of temperature and the more rapidly it takes place, the greater is the degree of hardness thus produced. Steel raised to a white heat and then immersed in cold mercury acquires a degree of hardness nearly equal to that of the hardest white cast iron or even of the diamond: it is then also extremely brittle. By heating such hardened steel and allowing it to cool gradually, it again becomes soft and less brittle. It is in virtue of this capability, which is one of the most distinctive characteristics of steel, that various degrees of hardness can be communicated to it, by regulating the temperature to which the hardened metal is heated before being allowed to cool gradually, or to which the soft metal is heated before being suddenly cooled. Steel tools and instruments are made and finished while the metal is in the soft state and the requisite degree of hardness is given to them as above described. This operation is termed tempering. The temperatures to which the metal requires to be heated in order to acquire, in this way, particular degrees of hardness are indicated by the yellow or bluish colours which the metal assumes by the formation of an extremely thin film of oxide on the surface.

By cooling the heated metal slowly these colours appear in the reverse order, and as soon as the required colour appears, the article to be hardened is plunged into the liquid in which it is to be cooled. This is generally water, but sometimes saline solutions are used, as well as oil, melted tallow, wax, etc.

The distinction between steel and cast iron or malleable iron is not by any means absolute; it consists rather in the degree to which considerable hardness or the capability of acquiring that character is associated with tenacity and malleability. Accordingly there are numerous varieties of steel approximating in various degrees to malleable iron or to cast iron. Together with such gradational differences in the characters of the metal, there are corresponding differences in the amount of carbon it contains; the closer the approximation to malleable iron, the smaller is the amount of carbon in the metal; the closer the approximation to cast iron, the larger is the amount of carbon. When the amount of carbon is less than about 0·65 per cent., the capability of being tempered is either wanting or very slight; when the carbon amounts to 1·75 per cent., the metal is capable of being made very hard, but its tenacity is much reduced. The capability of being hardened and tempered is associated with the maximum of tenacity when the carbon amounts to about 1·5 per cent. The opinion has long been entertained that these characters of steel are intimately connected with the amount of carbon it contains, but it is still unknown in what manner these facts are related. Cement steel contains from ·496 to 1·87 per cent. carbon, natural steel from ·985 to 2·44 per cent., soft steel ·95 per cent., the softest Bessemer metal ·08 per cent., and cast steel from ·86 to 1·94 per cent. In

Sweden several qualities of Bessemer metal are made, differing in the amount of carbon they contain, and distinguished by numbers as follows:

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Amount of carbon .	2·0	1·5	1·	·5	·05

The metal No. 1 can be forged, though with some difficulty, but it does not weld. On the contrary, No. 5 welds perfectly, but cannot be tempered.

The presence of silicon in steel is considered by some authorities to be advantageous so far as regards the capability of being hardened; but others are of opinion that it increases the tenacity of the metal at the ordinary temperature, and makes it difficult to weld, though a small amount of silicon renders steel soft. The best kinds of steel often contain only minute traces of silicon, and few contain more than ·02 or ·03 per cent.

Among the various substances which are frequently present in malleable iron and in cast iron, those which are most prejudicial to the quality of steel are sulphur, phosphorus, and copper. The amount of sulphur in steel of the best quality rarely exceeds ·012; within the limit of ·1 per cent. it is considered to render the metal more capable of being welded at a moderate heat, but to make it red short. Phosphorus also renders steel more capable of being welded and at the same time makes it cold short when it amounts to ·1 per cent. The best steel rarely contains so much. Copper renders steel decidedly red short when present in very small amount, and for this reason iron smelted from ores containing copper pyrites is not suitable for making steel.

The fact that certain kinds of iron ore containing manganese are especially suitable for the production of steel has given rise to the opinion that this metal is a necessary constituent of good steel; but it is in fact rarely the case that steel contains much manganese, and whatever beneficial influence the presence of that metal may exercise in the manufacture of steel would appear therefore to be of a totally different nature.

The presence of *chromium*, *nickel* or *rhodium* in steel is said to improve its quality, but the data on which the opinion rests are somewhat insufficient.

The results of the observations on the influence of *silver* upon steel are discordant. *Tungsten* and *titanium* have been stated to improve the quality of steel, but further experience is requisite in regard to this point. The steel of which the celebrated Damascus sword blades are made contains from ·05 to ·1 per cent. of tungsten, and it has been asserted that the presence of this metal increases the tenacity of steel and renders it especially suitable for cutting instruments. Four samples of tungsten steel analysed by Sievert contained from ·9 to 4·75 per cent.

The presence in steel of a minute amount of *nitrogen* as a necessary constituent has been alleged by Fremy; but Marchand, Rammelsberg, and Boussingault have failed to detect by their analyses any greater indications of nitrogen in steel than might fairly be ascribed to accidental sources. Caron infers from his observations that if steel contains nitrogen, it is not as an essential constituent, and similar results have been obtained by Baker and Stuart.

The colour of steel is greyish-white, sometimes almost pure white, and the hardened metal is sometimes whiter than the soft metal. The lustre of steel is not remarkably different from that of malleable iron. The surface of fracture presents a very fine granular texture, very uniform and without any of the fibre characteristic of good malleable iron. The fracture of hardened steel presents a remarkably close fine grained texture. Steel is always harder than malleable iron; but it is never so hard as that kind of white cast iron known as specular iron. The tenacity of steel is greater than that of either cast iron, malleable iron, or any other metal. According to the experiments of Muschenbrock and Rennie, it is at least twice as great as that of malleable iron; it is slightly reduced by hardening, but by annealing the metal the tenacity is rendered even greater than that of the unhardened steel.

The malleability of soft steel at the ordinary atmospheric temperature is even less than that of hard cast iron. Hardened steel is very brittle, and it will not bear working with the hammer. The malleability of steel is, however, considerably increased when the metal is heated.

The specific gravity of soft steel varies between 7·6224 and 7·8131. It is somewhat reduced by hardening the metal, viz. from 7·75 to 7·55 or from 7·79 to 7·67.

The specific heat of steel is 0·11848; its linear expansion when heated from 0° to 100° is scarcely greater than that of ordinary malleable iron, but it is less than that of cast iron. By heating from 30° to a red heat, a steel bar lengthens about $\frac{6}{560}$; the elongation of a bar of malleable iron within the same range of temperature is $\frac{4}{560}$, and that of cast-iron is $\frac{7}{560}$; by heating steel to whiteness, it lengthens $\frac{10}{560}$, and the corresponding expansion for malleable iron is $\frac{7}{560}$, that for cast-iron $\frac{12}{560}$.

When steel is heated to whiteness it becomes soft like ordinary malleable iron under the same conditions, and it is then capable of being wrought and welded, not

only to steel but also to ordinary malleable iron; steel welds, however, at a lower temperature than malleable iron does.

The melting point of steel is between that of cast iron and that of malleable iron; probably about 1800°, but the fusibility is influenced by the amount of carbon contained in the metal.

Steel is less susceptible of magnetic induction than pure iron, but it far exceeds iron in the capability of becoming permanently magnetic, for which reason it is generally used for making magnets.

Steel is oxidised much less readily than malleable iron by exposure to the atmosphere at the ordinary temperature, especially when it is polished and clean. When gradually heated in contact with atmospheric air, steel acquires as the temperature rises a succession of colours at the surface, from faint yellow to blackish blue. At 360° all colour disappears, but if the heat be raised still further, the colours reappear in the same order as before, but more faintly. The coloration is due to oxidation, and the change of colour is caused by the increasing thickness of the film of oxide, just as the succession of colours in Newton's rings is caused by the unequal thickness of a layer of air.

Hardened steel is dissolved by acids less readily than soft steel. With dilute hydrochloric acid or sulphuric acid, soft steel gives a larger amount of the black graphitic substance which is attracted by the magnet than malleable iron does. By the continued action of the acid, this substance is converted into a carbonaceous mass which burns without leaving any residue, as in the case of malleable iron and cast iron. With dilute nitric acid this graphitic substance is not separated from soft steel. Concentrated hydrochloric acid dissolves soft steel completely without residue.

The following table gives the composition of several kinds of steel:—

Kind of steel	Locality	Fe	Mn	Cu	Carbon		Si	S	P	Authority
					Combined	Graphitic				
Natural steel	Siegen	—	—	·379	1·698	—	·038	—	—	Karsten
,,	Solingen	—	—	—	1·570	—	·020	—	—	Lampadius
Puddled steel	Hartz	—	·012	—	1·380	—	·006	(Al ·12)	trace	Brauns
Cement steel	English	—	—	—	1·807	—	·100	—	—	Berthier
,,	German	—	—	—	·416	·080	—	—	—	Bromeis
Cast steel	Sheffield	—	—	—	·950	·220	—	—	—	,,
,,	,,	—	—	—	1·758		—	—	—	Karsten
,,	French	—	—	—	·65		·040	—	—	—
Sword steel	Damascus	—	·070	—	1·089		—	(Ni ·07 Wo ·1)		—
,,	,,	—	trace	—	·775		—	(Ni ·21 Co trace Wo trace)		—
Wootz	Indian	—	—	—	1·500		·600	—	—	—
,,	,,	98·092	—	—	1·333	·312	·045	(As ·037)	—	Henry
Cast steel	German	—	trace	·300	1·180		·330	(Ni ·12)	·020	—
,,	English	—	·024	·066	1·275		·213	(As ·007)	—	—
Bessemer metal	Dowlais	—	·576	·025	·490		·009	·033	·036	—
,,	Sweden	—	trace	—	·085		·008	trace	·025	Brusewitz
,,	—	—	·179	—	·300		·044	,,	·033	,,
,,	—	—	·256	—	·700		·032	,,	—	,,
,,	—	—	·464	—	·950		·047	,,	·032	,,
,,	—	—	·355	—	1·050		·067	,,	—	,,
Wired	Barrow-in-Furness	—	·214	—	·200		·179	·030	·026	,,
Rail heads	German	—	·386	—	·138		·306	·040	·034	,,
Rails	—	—	·264	—	·150		·091	·025	·032	,,
,,	—	—	·638	—	·046		·634	·045	·093	,,
Boiler plate	—	—	·136	—	·250		·016	·010	—	,,
—	—	—	·273	—	·300		·056	·040	·041	,,

ORGANIC CHEMISTRY.

SUBSTANCES DERIVED FROM PLANTS AND ANIMALS.

The material of which plants and animals consist comprises a great variety of distinct substances, some of which are constant constituents of all plants or animals, while others are peculiar to certain species or to particular organs of plants and animals (*ante*, p. 67). Apart from the phenomena of reproduction, growth and development by which plants and animals differ from minerals, the substances of which they consist differ in their general character very widely from those treated of in the preceding part of this work. These substances are also remarkable from a chemical point of view on account of the general similarity of their composition, since they all consist either of carbon, hydrogen and oxygen, or of these elements together with nitrogen, sulphur, or phosphorus, while some consist simply of carbon and hydrogen. Many of them contain exactly the same elements combined in the same proportions, but are nevertheless totally different substances.

Under ordinary conditions the formation of these substances is incidental to the performance of those functions of plants and animals which collectively constitute the phenomenon of life, and on account of this peculiarity the substances formed in the organisms of plants and animals are termed organic substances, while those which do not originate in this way are distinguished from them as inorganic substances. (See p. 15, and Carbon Compounds, pp. 67, 69.)

Until recently it was supposed, not only that the constitution of organic substances was essentially different from that of inorganic substances, but also that their formation was the result of special influences, of a nature altogether distinct from those to which ordinary chemical action is due. These suppositions are now abandoned, and the substances produced by plants and animals are regarded as being in no way essentially distinct, as regards their origin and constitution, from those commonly termed inorganic substances.

It is in the plant organism chiefly that the formation of organic substances takes place, and the chemical activity of the animal organism is characterised rather by the transformation of substances derived from plants.

All the organs of plants are formed by the aggregation of numerous elementary parts differing in form, characters, and composition. These elementary parts are called cells; the combination of cells is termed tissue.

Cells in their simplest form are minute vesicles closed on all sides, consisting of various organic substances partly nitrogenous and partly non-nitrogenous; they also contain mineral constituents, and so long as they exercise the functions of life they are charged with water.

The young organs of vegetation, such as the germ, the embryo, the young rootlet, and the cotyledons, consist of cells with extremely delicate walls, which enclose—chiefly, and in greater proportion than the other tissues of plants—organic compounds consisting of carbon, hydrogen, oxygen, nitrogen, and sulphur. These substances are very similar in composition and properties to those forming the principal part of the animal body. They are classed together under the term albuminoids. The young organs of plants, besides being very rich in albuminous substances, also contain a very large proportion of mineral constituents which remain as ash when the organic portion is burnt.

The albuminoids of the vegetable cell are saturated with water, presenting the appearance of a viscid material insoluble in water and mixed with granular concretions. This material constitutes the protoplasm of the cells, and it is the seat of the chemical changes, such as the formation of cellulose or the substance of which the cell-membrane consists.

The cells are formed in the midst of the juices which permeate the plant, and as they are successively developed become agglutinated together with the cells previously produced. The original spherical form of the cells often becomes modified in consequence of the pressure attending this agglutination; and sometimes they form in this way elongated tubes communicating at their contracted extremities, as shown in the longitudinal section of the asparagus (fig. 428; fig. 429 being a transverse section): they then form what is called vascular tissue, other illustrations of which are to be found in hemp and cotton fibres.

As growth proceeds, the cells contained in the seed alter their form and arrangement in the most diverse manner. They change into cells of other kinds, elongated cells unite by fusion of their outer surfaces into tubes and vessels; in many cases the extremely delicate cell membrane thickens considerably by the deposition and accumulation of various substances. But whatever change of form may take place, whatever shape or size the vessels or tubes may assume, the material forming their envelope

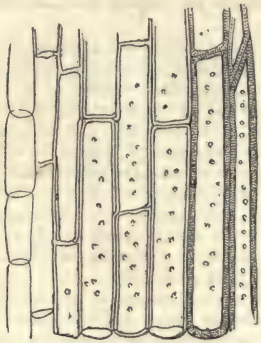


FIG. 428.

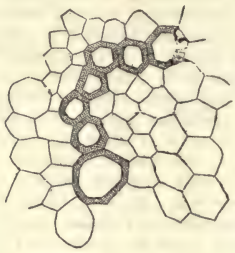


FIG. 429.

remains always the same. This is cellulose, or, as it is sometimes called, lignin, an organic substance consisting of carbon, hydrogen, and oxygen. The relative proportions of the elements in this substance are such that the hydrogen and oxygen bear the same ratio to each other as in water; hence cellulose and bodies of similar composition are classed together under the term carbo-hydrates.

The epidermis or external envelope of plants consists of cells the walls of which have become very much thickened, and the cellulose partly changed and partly impregnated with various substances, such as fat, albumin, salts of calcium, and silica. When the epidermis is detached or injured, the underlying tissues acquire the character of the epidermis cells, and by absorption of those substances become changed into cork tissue.

The thin elongated cells which constitute cotton and are the seed hairs of the cotton plant, as well as the cells thickened by concentric layers in the fibres of hemp, flax, *Phormium tenax*, *Agave americana*, *Urtica nivea*, etc., consist of nearly pure cellulose. In the cells and vessels of woody tissue the cell membrane, originally consisting of cellulose, is thickened by the gradual deposition and alteration of repeated layers of cellulose; it is thus converted into woody fibre, and is, moreover, impregnated with colouring matters, resin, etc. In algæ and lichens the cellulose is penetrated with lichenin. In some cases the membranes of individual cells are cemented together with pectose, pectin, pectic acid, or the calcium, potassium, or sodium salts of this acid; as, for instance, in the epidermis tissue of the *Cactaceæ*, in the vascular tissue of hemp and flax, as well as in the parenchyma of the succulent roots, tubers, or rhizomes of carrots, sugar beets, potatoes, and some fruits.

By suitable treatment these foreign substances can be separated from cellulose. For this purpose it is sufficient to macerate thin slices of the roots, etc., for about a fortnight in hydrochloric acid diluted with ten times its volume of water, then to wash them with water, afterwards with dilute ammonia, and finally again with water. The cellulose can thus be almost entirely deprived of most foreign ingredients.

The woody fibres which constitute the greater part of the pith and sap wood of trees are not cemented together with pectin substances.

The substance, which permeates the cellulose in wood and is called by Payen incrusting material, is an amorphous, hard, brittle substance of complex composition, richer

in carbon than cellulose; the proportion of hydrogen to oxygen is greater than in water and in the carbo-hydrates. It occurs in the hard masses of the bark of trees, in certain hard concretions of fruits—especially pears—in the shells of nuts, and in the stones of fruits. The amount of this substance in the different kinds of wood varies.

The hardness, weight, and brittleness of wood are due to incrusting materials. The greater amount of carbon and hydrogen in wood, as compared with cellulose, is likewise due to their presence. These substances are accompanied by colouring matters and by albuminoids, which are the remains of the protoplasm of the young cell. The younger the wood the less incrusting materials it contains, and the richer it is in unaltered cellulose and albuminoids.

Each fibre of woody tissue is enveloped with a solid albuminous material which, when moistened with iodine solution, gives no reaction with sulphuric acid; and on this account woody tissue does not give the cellulose reaction, or but indistinctly, until the foreign substances have been got rid of.

The mineral substances present in plants are not accidental, they are found partly in the cell membrane, partly in the juices of the cell, partly deposited in certain parts of plants, such as the epidermis or in the interior of the tissues.

Thus calcareous secretions are often found in the leaves of the *Urticaceæ*, in the spongy cell membranes of the seeds of various sorts of *Celtis*, in some of the *Characeæ*, and in the incrusted tissues of *Corallina*.

Crystalline concretions occurring free in the cell are termed raphides. Such concretions of calcium oxalate are very frequent in phanerogamous plants, especially in the leaves round the bundles of vessels forming the veins of the leaf. They also occur in the branches, and are very plentiful under the layers of epidermis in the cellulose tissue of the *Cactaceæ*.

The presence of calcium carbonate in such concretions was shown by Payen in 1845. Before that time it was thought that the earthy carbonates always found in the ash of plants were produced by the decomposition of salts of organic acids. Although the greater part of the carbonates in the ash is undoubtedly thus produced during combustion, the existence of calcium carbonate in the plant has been confirmed by others. Some parts of plants are so rich in carbonates that their presence is easily recognised. If ten or twelve seeds of *Celtis orientalis* are placed in a test tube and covered with diluted hydrochloric acid, brisk effervescence takes place owing to the escape of carbonic acid; which, if the test tube be closed with a soft cork, is strong enough to drive out the cork after a short time. According to Payen, these seeds contain as much as 40 per cent. of calcium carbonate.

The accumulation of considerable masses of mineral substances to form such concretions is, however, to be regarded as exceptional, but all parts of plants contain mineral constituents to some extent; indeed, no cells can be formed without a sufficient supply of mineral substances.

Seeds, spores, fungi, and the germs and buds of the more highly organised plants, contain, besides cellulose or one of the substances analogous to it—such as starch, dextrin, inulin, gum, sugar, mannite—other substances, such as albuminoids, fat, earthy phosphates, alkalies, silica, and water, which are all necessary for their development and for the exercise of their vital functions. Precisely the same conditions prevail in the egg of an animal and in milk, which is the first food of the young mammal; both in the egg and in milk, as in the case of plants, there are albuminoids, saccharine substances, fat, and mineral constituents. These are the food upon which both animals and plants subsist during the first period of development or of germination.

The following table gives the composition of a few plants when dried:

	Morels	Mush-rooms	Beer Yeast	Truffles	Cauli-flower
Albumin	44·0	52·0	31·36	62·7	66·0
Fat	5·6	4·4	2·00	2·1	4·5
Mannite, dextrin, cellulose, etc.	36·8	38·4	59·25	29·4	18·3
Earthy phosphates, alkaline chlorides, silica, etc. .	13·6	5·2	7·39	5·8	11·2
Amount of water in the fresh state	90·0	91·0	90·00	72·0	90·7

* The amount of carbon in most parts of plants varies from 48 to 54 per cent., while cellulose, as already mentioned, contains only 44·4 per cent. This excess in the amount

of carbon in plants as compared with cellulose is caused by the deposition of substances richer in carbon than cellulose, such as resin, albumen, fat, etc. These substances are not only richer in carbon than cellulose, but they also contain proportionally more hydrogen; and therefore in plants there is always an excess of hydrogen relatively to oxygen, the conditions in regard to the amount of elementary constituents being the same in the entire plant as they are in the cells.

The elementary substances which always occur in all plants are carbon, hydrogen, oxygen, nitrogen, sulphur, potassium, sodium, calcium, magnesium, iron, phosphorus, silicon, and chlorine. Besides these, which must be considered as essential constituents of plants, there have been found in certain plants rubidium, cæsium, lithium, barium, aluminum, manganese, zinc, bromine, iodine, and fluorine, which may be regarded as incidental. The former must be supplied to the plant if new vegetable substance is to be formed, whilst most plants are able to attain their full growth without the presence of the latter; therefore, the elements of the first-mentioned group in various states of combination form the food of plants.

As regards assimilation of nourishment plants vary. The lower kinds, as well as the most highly organised, during the period of germination require, as already mentioned, ready-formed organic material for their nutrition. Fungi obtain this from the substratum upon which they live; the germinating embryo of the seed and the sprouting buds of the tree, however, obtain this organic material from a store laid up during the previous period of vegetation in the tissues surrounding or accompanying the embryo or the bud.

But it is quite another thing in the plants provided with green organs or in the young shoot as soon as it has developed green leaves. When this is the case, the most simple compounds of the requisite elementary substances serve as food, as in the case of every plant provided with foliage. These food elements consist of carbonic dioxide, water, nitric acid, ammonia, sulphuric acid, phosphoric acid, potash, sodium chloride, lime, magnesia, oxides of iron, and silica.

On examining the cells of the leaves of the higher organised plants there are found, close under the epidermis, numerous cells, in the protoplasm of which is a granular green substance called chlorophyll, to which the leaves owe their colour.

This substance possesses the property, by the aid of light and warmth, and when the other materials of plant food are present, of decomposing carbonic acid and water, with disengagement of oxygen, and converting these inorganic substances into organic material.

Green plants produce organic substances out of inorganic substances, while plants that do not contain chlorophyll use organic material to build up their structure. There is, however, a further difference: plants that do not contain chlorophyll not only use organic substance for the building up of their own body, but they also decompose a part of that substance and convert it into carbonic dioxide, while green plants decompose carbonic dioxide and produce organic substances. The greater part of the dry substance of plants consists of carbon, and therefore above all other forms of food carbonic dioxide must be supplied to plants in the largest quantity. The atmosphere affords a constant supply of this gas, and from that source plants obtain all that they require of this material. The relative amount of carbonic acid in the atmosphere as compared with its other constituents is certainly small, but the absolute quantity is so considerable that it would suffice for sustaining vegetation many years if the whole surface of the earth, not only our gardens and fields but also all sterile places, and the entire surface of the sea, were covered with the most luxurious vegetation.

Those plants or parts of plants which serve as food for man and animals are, for the most part, burnt in the animal system, and their carbon again converted into carbonic dioxide; whatever portion does not undergo this change passes after some time into decay. When either plants or animals die the same kind of decomposition takes place, and all the carbon of the organic substance is converted into carbonic dioxide. Vegetable materials, either of modern growth or those belonging to a former age, when burnt as fuel also give back their carbon as carbonic dioxide to the atmosphere.

Thus plant life and animal life maintain a constant balance. Animals require for their existence oxygen, and they discharge carbonic dioxide into the air. Plants abstract carbonic dioxide from the atmosphere, and maintain the latter in a state respirable by animals by returning to it oxygen.

All the green parts of plants possess the power of assimilating carbonic dioxide. Plants which live immersed in water behave just in the same manner as those that grow on land. They derive their carbon from carbonic dioxide, which the water animals expire, and they thus render the water habitable by animals.

Hydrogen and water are abundantly furnished to plants by rain and the water

vapour present in the atmosphere. Nitrogen, although it exists abundantly in the free state in the atmosphere, is not thus assimilated by plants. Besides free nitrogen, however, atmospheric air contains two compounds of nitrogen, viz. ammonia and nitric acid. From both these substances plants obtain the nitrogen from which they produce albuminoids and their other nitrogenous constituents. Rain and dew collect the ammonia and nitric acid contained in the air and carry them into the soil, from whence the roots of plants absorb them. The remains of human and animal food are supplied to the earth as manure, and all dead bodies of animals are returned to it. By the process of decomposition and decay nitrogenous organic compounds are transformed into ammonia and nitric acid, just in the same way as carbon is converted into carbonic dioxide. By thus returning to the soil all materials capable of decomposition, the soil is supplied with substances which serve again for a new generation of vegetable life. Thus, destruction and reproduction go hand-in-hand. Material existence is in a constantly uninterrupted cycle of change from life to death and from death back again to life.

In consequence of the source from which carbonic dioxide, water, ammonia, and nitric acid are chiefly derived, these substances are termed the atmospheric food materials of plants.

All other essential ingredients of plant food are derived from the soil. That soil only can be fertile in which all the nutritive substances are contained; its productive capacity is determined by the amount and state of combination of the food materials it contains It is not sufficient that the elements above-mentioned are present in the soil, but they must also be present in such a condition that plants can easily absorb them. The substances present in rocks acquire that condition by the process of weathering under the disintegrating influences of the atmosphere and water, which not only break up their state of aggregation, but also alter their chemical composition, so that their constituents can be absorbed by the roots of plants. As a consequence of this weathering some of the constituents of the soil are rendered soluble in water, or in water containing carbonic acid, while others remain insoluble.

All the materials of plant food are equally important, although it is true that in all kinds of plants the quantity of constituents derived from the soil is less, and frequently much less, than the other part of them; still it is not possible for any plant, or even the smallest organ of a plant, to be formed when they are wanting; even when a single constituent fails the remainder are worthless. Therefore vegetation is only possible when all are present together, and the productive capacity of land is determined by that food material which it contains in the least quantity. It is thus clear that, in virtue of the weathering process continuing from year to year, the fertility of land could be maintained by returning to it all the constituents of the plants grown upon it. This, however, does not generally happen. Each year a great quantity of plant material is produced in the form of corn, milk, meat, etc., which is consumed in large towns; and, instead of being returned to the land again, the products contaminate the soil and the atmosphere of the towns, as well as the rivers into which the drainage of the towns is discharged. Not only in this respect do injurious results follow, but the continual drain upon the land where those materials were grown causes it to become poorer in the food materials which are necessary for the growth of plants. This impoverishment of the soil can be prevented either by returning to the land the refuse of towns, or by giving back to it in another form the food materials of plants.

The proximate organic constituents of plants, in the free state or chemically combined, generally occur in various amounts in the individual organs, while some are found especially in particular tissues. Thus the albuminoids, together with some other nitrogenous and mineral substances, preponderate in the young growing organs; cellulose preponderates in the cell membranes, which are more delicate the younger the tissues and the greater the vegetative activity in them.

Sugar exists as an aqueous solution in the parenchyma of the cells, deposited round the fibro-vascular bundles, as in the sugar cane or sugar beet.

Starch is found in similar tissues, as in the potato.

Lignin penetrates and thickens especially the cell membranes of woody tissue, which in the early state consist of pure cellulose.

Various ethereal oils, resins, and balsams are secreted in the glands, reservoirs, and ducts of the plant.

In the ice plant (*Mesembryanthemum crystallinum*) oxalates of sodium and potassium in alkaline solution fill numerous glands of the leaves and branches.

One or two rows of cells situated immediately below the epidermis of the seeds of the *Gramineæ* are filled with drops of oil or albumin. The cotyledon of the same seed exhibits a large number of cells, the contents of which consist of oil and albumin.

The cotyledons of the seeds of the so-called oil fruits are especially rich in cells

containing oil and albumin. Seeds generally are rich in albuminoids, and these are always accompanied by fat, or starch, and the mineral food of the plants.

Those branches of industry embracing the manufacture of organic substances aim generally at the extraction of the constituents of plants and animals (textile fibres, starch, sugar, fats and oils, alkaloids, organic acids and dye stuffs, albumin, gelatin, etc.), or at the conversion of vegetable and animal substances into other products (dextrin, grape sugar, bread, wine, beer, alcohol, and vinegar, soap, leather, etc.).

Between the various groups of organic substances certain broad distinctions and relations exist, and thus a sort of classification is possible.

First in order, from their simplicity of composition, come the essential oils; these consist for the most part of liquid hydrocarbons having the same composition as turpentine $C_{10}H_{16}$, but including several allotropic modifications. Other oils are composed in part of a mixture of these or one of them, with polymeric modifications of the composition $C_{15}H_{24}$, while a few contain also $C_{20}H_{32}$. Most essential oils also contain oxidised substances, which generally partake of the nature of camphors $C_{10}H_{16}O$, and associated with these are still more highly oxidised bodies, as gums and resins. The fixed oils and fats come next in order of simplicity of composition; they genera lly contain oleic acid $C_{18}H_{34}O_2$ and allied compounds, while the fatty acids $C_nH_{2n}{\cdot}O_2$ sometimes occur in the free state. More often, however, the fatty acids are in combination as glycerides or ordinary fats, such as stearin $C_3H_5(C_{18}H_{35}O_2)_3$.

The different kinds of sugar and starch are also made up of carbon, hydrogen, and oxygen, the two latter elements being present in the same proportions as in water; hence these substances are termed carbon-hydrates. Thus, cane-sugar is $C_6H_{12}O_6$, and potato starch is $C_6H_{10}O_5$. Cellulose and such substances are allied to starch.

The organic acids constitute another group of substances, presenting no features of composition in common, beyond their nature as acids, as in the case of tartaric acid $C_4H_6O_6$; malic acid $C_4H_6O_5$; citric acid $C_6H_8O_7$; meconic acid $C_7H_4O_7$; gallic acid $C_7H_6O_5$, etc. Allied to gallic acid is tannic acid, and this latter substance is closely related to tannin, which in its natural state is said to be a glucoside. Glucosides are met with widely in organic nature, and may be split up into glucose and acids or other substances, just as fats split up into glycerine and acids.

The colouring matters or dye stuffs are partly oxidised compounds, such as alizarin $C_{10}H_6O_2$; while yet others are also nitrogenous in nature, as indigo blue (C_8H_5NO).

Again, the alkaloids are nitrogenous compounds, as for instance quinine $C_{20}H_{24}N_2O_2$, and morphine $C_{17}H_{19}NO_3$.

More complex in constitution are the substances allied to albumin, which occur in both plants and animals. All of them contain nitrogen and a few contain sulphur, but they possess in common a distinct relationship to one original form which has a formula $C_{72}H_{112}N_{18}SO_{23}$.

Another group of organic substances occurring less widely than the albuminous principles, but possessed of equal complexity of constitution, contain another element, viz. phosphorus, but no sulphur. These substances occur in the nervous tissues of animals, and resemble in general structure the fats, but differ in being nitrogenous and phosphorised. An instance of this kind is presented by lecithine $C_{42}H_{84}NPO_8$, which occurs in the yelk of eggs and in the brain. Such substances as those just described are found in combination with salts, a feature due to their partly alkaloidal nature.

CELLULOSE.

The substance of which the solid framework of plants consists has received this name from its origin in the form of cells. The physical properties of cellulose vary according to the internal arrangement of the particles. In Iceland moss they are so loosely aggregated, and moreover their cohesive power is so weakened by the deposition of inulin between them, that upon simply boiling the moss with water the cells swell up and disintegrate, forming a liquid which gelatinises on cooling. The cellulose in this gelatinous mass is coloured blue by iodine, a reaction which is also exhibited by a few other lichens, by the tissues of a number of fungi, and by the very thick membranes of the leaf cells of several Aurantiaceæ.

This coloration by iodine has given rise to the assumption that, in such cases, the substance is different from ordinary cellulose, and it has been called lichenin, and it was further assumed that this substance was converted into a gum-like substance by boiling it with water. The liquid contains, however, no gum, since it does not yield mucic acid when treated with nitric acid. There is indeed no sufficient reason for assuming that the substance called lichenin is specifically distinct from cellulose, rather than one of the numerous modifications of cellulose, all of which differ merely in the arrangement of the cellulose molecules.

The substance of the cells in other plants has a very different character. The inner shell of the cocoanut, and the fruit of *Phytelephas macrocarpa* (vegetable ivory), have cells with thick walls of an almost stony consistency. To this property vegetable ivory owes its name, and its application to articles of turned and carved work.

The woody fibre of trees, as above mentioned, consists in part only of cellulose, and, according to the age of the cells, is more or less incrusted with other substances,

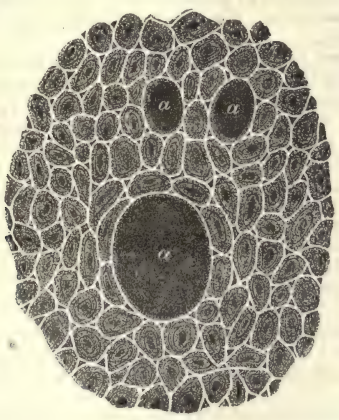


FIG. 430.

as shown in fig. 430, which represents a section of oak wood. The dark spaces (*aaa*) are large sap-conducting vessels.

Composition.—Cellulose has the same percentage composition as starch, dextrin, inulin, etc., containing:

Carbon	44·44
Hydrogen	6·18
Oxygen	49·38
	100·00

It is, therefore, isomeric with those substances. Its composition is always the same from whatever plant, or part of a plant, it is obtained, and it is represented by the formula $C_{12}H_{20}O_{10}$.

Characters.—Cellulose when pure is a white translucent substance, insoluble in water, alcohol, ether, fats, or ethereal oils. Its specific gravity is about 1·5.

Dilute aqueous solutions of caustic alkalies and dilute acids do not affect moderately compact cellulose even by protracted boiling. Concentrated sulphuric or phosphoric acid decomposes cellulose even in the cold, converting it first into a substance resembling starch, then into dextrin, and finally into grape sugar. Very strong nitric acid converts cellulose into pyroxylin, or gun cotton. (See p. 227.)

Strong oxidising agents, such as chlorine and the hypochlorites, effect the oxidation of cellulose even in the presence of water. When paper pulp, or filter paper torn to shreds, is digested with a saturated aqueous solution of bleaching powder, and the mixture slightly heated, a very violent reaction takes place, which continues even after the source of heat has been removed. The cellulose is disintegrated and oxidised, carbonic acid being copiously evolved. The destruction of linen and other organic tissues in bleaching, by the inconsiderate use of bleaching powder, is due to this cause.

Pure cellulose is not altered by exposure to atmospheric air, but, as it occurs in wood and the ligneous tissues of plants associated with albuminous and resinous substances, it undergoes gradual alteration, and is converted, probably by oxidation, into a friable substance of a yellow or brown colour called touchwood.

Cellulose shows a characteristic behaviour when treated with iodine and sulphuric acid. If cotton, paper, or any vegetable tissue consisting of pure cellulose be moistened with an aqueous solution of iodine, and a drop of concentrated sulphuric acid be then added, a blue coloration is instantly produced. This reaction is also characteristic of starch, therefore it may be assumed that, in the case of cellulose, the reaction is due to the conversion of cellulose into a substance allied to starch by the action of the sulphuric acid. However, some other substances beside starch show the same reaction when treated with iodine and sulphuric acid.

The facility with which cellulose may be prepared in a state of purity depends upon the raw material operated upon. The easiest method of obtaining pure cellulose is to separate it from white cotton, unsized white paper, or old linen. For this purpose the material is boiled for an hour with a dilute aqueous solution of potash or soda (containing about 5 per cent. of alkali), it is then washed with water, and boiled with an equally dilute solution of sulphuric acid, again washed with water, and finally washed with alcohol and ether. The cellulose obtained by this means is contaminated only with traces of silica.

It is far more difficult to obtain pure cellulose from wood, or the woody tissues of plants. It is necessary to boil the wood first with a solution of bleaching powder, then to wash it with water, boil it with a strong solution of potash, and evaporate the liquid to dryness; the undissolved portion is again treated with bleaching powder, these operations being repeated successively until the substances incrusting the wood, such as lignin, nitrogenous matters, colouring matters, fats, etc., have been removed. This method, however, causes considerable loss of material, owing to the action of chlorine and potash upon the cellulose.

According to Fr. Schultze very pure cellulose may be obtained as follows. The raw material is digested in the cold for a length of time, varying from a fortnight to three weeks, with a mixture of 8–10ths of its weight of potassium chlorate, and 12 parts of nitric acid of specific gravity 1·100. The mixture, in order to avoid explosion, should not be heated. A bleached mass is thus obtained, which is washed first with cold water, and then continuously with boiling water, afterwards digested with dilute ammonia, again washed with water, and finally washed with alcohol and ether. Though the cellulose remains intact by this process, it is not always possible to decompose all the lignin.

Cellulose may be also obtained from the solid excrements of animals, especially the ruminants. The individual tissues are in this case destroyed by mastication, and a number of foreign substances are extracted by the process of digestion. The finer and more loosely aggregated particles of cellulose are dissolved by the digesting process, and absorbed by the body of the animal, while the more solid portions, the layers of epidermis, the vascular bundles, and the woody tissue, pass into the excrements.

Cellulose is dissolved by an ammoniacal solution of oxide of copper. A solution of this kind may be prepared in different ways. Peligot prepares it by oxidising copper turnings in contact with ammonia; a glass tube open at both ends is filled with copper turnings that have been oxidised on the surface by heating to redness and then reduced in a stream of hydrogen, and a very strong solution of ammonia gradually

dropped upon the copper turnings. The blue solution thus formed is passed once or twice more over the copper turnings so as to complete its saturation.

Cellulose, as it is contained in unsized paper, swells up and very soon dissolves. A solution of ammonium cuprate, containing from 3 to 4 per cent. of cellulose dissolved in it, has a viscous consistency. In order to separate undissolved substance, and obtain a clear solution of cellulose in ammonium cuprate, an asbestos filter must be employed for filtering it.

By the addition of dilute hydrochloric acid to the clear solution of cellulose in ammonium cuprate, the cellulose is precipitated in a pure state.

Cellulose thus prepared, when examined under the microscope, exhibits granular flakes of an indefinite form. In spite of the extraordinarily fine state of division of cellulose thus prepared, it is not converted into the starch-like modification; it is chemically unaltered, and is not coloured blue by iodine until first acted upon by sulphuric acid.

If cellulose held in solution by ammonium cuprate is in a state of chemical combination, the combination is certainly of a very unstable nature, for a solution of this kind merely requires diluting with water to cause the separation of cellulose. Or further, if to a moderately diluted solution hydrochloric acid be added, drop by drop, so as to partly neutralise the great excess of ammonia, cellulose is likewise precipitated. When thus precipitated cellulose, according to Payen's researches, is not pure, but always contains copper.

When vegetable tissues are treated with a solution of ammonium cuprate the parenchyma cells and the cell nuclei easily dissolve, while the epidermis, the cuticle, and the woody fibres, are not affected, on account of the presence of incrusting substances.

Different substances behave differently when treated with a solution of ammonium cuprate, which may be seen from the following *résumé*:

The pure cellulose of textile fibres dissolves, and is precipitated upon saturating the solution with acids.

Mucilage, a body isomeric with cellulose, behaves like cellulose.

Gluten dissolves completely.

Fibrin swells up, dissolves completely after standing 36 hours; upon saturating the solution with an acid 93 per cent. of the fibrin is precipitated, a part being decomposed.

Albumen—coagulated white of egg—swells up, dissolves completely in 3 days; upon saturating with acid only 53 per cent. is precipitated.

Gelatin, softened in water, is dissolved in a few seconds, and no precipitate is formed on addition of acid to the solution.

Wool swells up, disintegrates, is mostly dissolved after a space of 6 days; upon saturating the solution with an acid only 16 per cent. separates out.

Hair behaves like wool.

Horse hair dissolves to the extent of 94 per cent., of which 38 per cent. is precipitated upon saturating the solution with an acid.

Horn dissolves completely, 16 per cent. being precipitable by acids.

According to Schlossberger *cotton*, dissolved in ammonium cuprate and treated with a concentrated solution of common salt, becomes, after a time, insoluble, and after washing and drying is coloured blue by iodine. Not only do acids effect the precipitation of cotton dissolved in ammonium cuprate, but gum, dextrin, grape sugar, etc., also precipitate cotton from such solutions.

Amorphous cellulose is more easily converted into dextrin and sugar than the unaltered cellulose of cotton.

This different deportment of cellulose under different conditions serves to show what entirely different properties the same substance may assume, according to its organised structure and the state of molecular aggregation.

Cellulose can also be distinguished by chemical means from other constituents of textile fibres. A solution of nickel oxide in ammonia dissolves silk but not cellulose; therefore, in mixed tissues, cotton, linen, and hemp remain unaltered by this reagent.

Uses.—The cellulose of cells with delicate walls, since it is digested by animals, must be considered as an article of nourishment playing the same part as starch in the animal economy; but it is not known what secretion of the animal system effects the digestion of cellulose.

Cellulose in the form of long-extended cells forms the chief constituent of the textile fibres known as flax, hemp, cotton, and the fibres of *Agave americana*, *Phormium tenax*, banana, *Böhemeria utilis*, *Urtica nivea*, etc., which are used in the manufacture of string, ropes, textile fabrics, paper, pasteboard, etc.

Another application of cellulose is in the preparation of oxalic acid. For making this acid sawdust is evaporated with a very strong solution of potash, and the residue then strongly heated. The mass contains potassium oxalate.

Animal Cellulose (Tunicin).—While the epidermis of all the higher organised animals, as well as all their tissues, consists of very nitrogenous material, the epidermis of low organised animals is proportionately poor in nitrogen, and a non-nitrogenous substance having the composition of cellulose can be separated from it. This substance was discovered by C. Schmidt, whose observations were confirmed by Loewig and Köllicker. The brown mantle of the *Tunicata*, the covering of *Phallusia manillaris*, the cartilaginous covering of the *Ascidiæ*, the mantle of *Cynthia*, all yield, when treated in succession with hot water, alkalies, acids, alcohol, and ether, a white substance which retains the shape of the material employed. This substance is animal cellulose, or *tunicin*. Although its composition is the same as that of cellulose obtained from plants, and although both have many properties in common, it is still questionable whether they are identical, and tunicin certainly possesses properties which distinguish it from vegetable cellulose. According to Berthelot it is coloured yellow by iodine, and it is difficultly soluble in ammonium cuprate; again, vegetable cellulose is carbonised by boron fluoride, while tunicin is not attacked by that reagent.

Animal fibres are distinguishable from vegetable fibres by their more complex chemical composition. Thus, wool is an albuminous substance, and contains a large amount of nitrogen and some sulphur; silk contains no sulphur. Animal fibres dissolve easily when boiled in a solution containing from 5 to 10 per cent. of potash, while the more compact cellulose of the vegetable fibres is unaltered. In order therefore to determine whether a fabric consists of wool or silk alone, or mixed with cotton, flax, or hemp, it is only necessary to boil a small piece for a short time in a weak solution of potash. If the fabric consists of pure silk or wool it is completely dissolved; if it contains other fibres they remain undissolved. In order to determine the proportion between these fibres it is best to cut out from the fabric a piece of a definite size, and to count the individual fibres. The piece is then boiled with the solution of potash, and when the animal fibres are dissolved it is washed and dried, and the fibres left intact are counted. The difference between the number of fibres before and after boiling gives the amount of wool and silk fibres, the remainder the number of the vegetable fibres. In undyed materials the percentage by weight of both kinds of fibres may be determined by drying and weighing the piece of fabric in question in a closed vessel before boiling with potash, and again weighing it after washing and drying.

Wool and silk, when occurring together, may be distinguished by treating the fabric containing them with a solution of potassium plumbate, prepared by dissolving 10 parts of potash in 100 parts of water and boiling it with 15 parts of litharge; the piece of fabric is plunged into the cold solution of potassic plumbate. All substances containing sulphur, such as wool, horn, hair, skin, nails, muscles, albumin, etc., assume a brown colour, while substances that do not contain sulphur, such as silk, bones, glue, chitin—a substance contained in the wing-cases of beetles and in the carapace of crabs—ivory, gelatin, etc., are not coloured by this reagent.

For detecting cotton, wool, and silk, in mixed tissues, they are boiled with concentrated hydrochloric acid. Cotton is completely destroyed, being partly dissolved and partly rendered so brittle that it can be separated as dust from the remaining mass after washing and drying. This residue is then placed in cold strong nitric acid, which dissolves the silk in a few minutes, while the wool remains comparatively unaltered.

The fibres of New Zealand flax (*Phormium tenax*) and of jute (*Conchorus capsularis*), when occurring in the same fabric together with hemp and flax, may be recognised by the curious behaviour of the nitrogenous constituents of the former. The piece of fabric to be examined is plunged for a moment into red fuming nitric acid, of a specific gravity of 36° B.; New Zealand flax (provided it was not before completely bleached) is at once reddened. The following reaction is still more characteristic. Pieces of the yarns or fabrics to be tested are dipped in a saturated solution of chlorine. In the case of fabrics, warp and woof ought to be isolated by drawing out a few fibres from the edges of the piece in order to liberate the two crossing threads. After the pieces have remained a minute in the chlorine water they are taken out, placed upon a flat plate, and covered with ammonia, which produces characteristic colorations. The fibres of jute and *Phormium tenax* assume a red colour which rapidly darkens, and in about a minute passes into brown; cotton and linen assume, according as the flax has been more or less steeped, a yellow, orange, or brownish hue, which cannot be mistaken for the coloration assumed by the New Zealand flax. Of course these reactions can only take place when the fibres have not been previously fully bleached, for the pure cellulose of these fibres does not behave in this way either with chlorine and ammonia or with nitric acid; the reaction is entirely due to the foreign substances present in the fibres.

The fibres of plants as already stated are connected together with pectates and albuminoids, and always contain some remains of protoplasm. To destroy these and to set the fibres free is the object of steeping or retting. This operation is

attended with various evils, such as the contamination of streams and the destruction of fish, the charging of the air with disgusting smells, etc. A new method discovered in America by Schenk obviates all these nuisances, and seems likely with a few improvements to give a new direction to the preparation of flax and hemp.

The flax is grown upon a dry—if necessary, drained—and manured soil, and is with advantage drilled in rows. The crop must not be got in too late, the seeds must still be soft, the stalks yellow below, but from the middle upwards still green. After plucking, the plants are laid in rows in an inclined position against one another, in order to ripen. The seed perfects itself at the expense of the sap still contained in the plant, the fibre obtains great firmness, and a slow drying of the plant takes place from below upwards. Passing showers do the plant no harm.

The flax bound in bundles is then carried to the dressing-house, where it is stored up in barns or sheds for further treatment.

There the first operation is the collection of the seeds. For this purpose the stems are grasped in the hand, and placed, with the lower end foremost, between a pair of revolving rollers. In passing through these rollers the fragile seed capsules are crushed and the seed falls into a chaff machine, where it is freed from the remains of the capsules. The rollers employed are of cast iron and hollow, having each a diameter of 6 to 8 inches; they are set one above the other, and the lower one alone receives a rotatory motion, while the upper one acts by its weight alone.

After separation of the seeds, the next thing is to separate the stems from the roots. For this purpose the bundles, just as they come from the rollers, are beaten between the hands upon a table, so as to get them in an upright position; in this position the lower portions are held in a kind of chaff-cutting machine, which separates the stems from the roots. There then follows an accurate sorting out; the bundles are loosely strewed upon a table, and the too short or too thick stems are removed. Three sortings can be made with advantage, each of which is afterwards worked up for itself.

The retting process is carried out in a water tank with a false bottom. The stems, once more arranged together in bundles, are placed upright upon the false bottom; when the vat is nearly full up to the margin with the stems, a wooden trellis or grating is laid over them, and the vat is completely filled with water, having a temperature of 36° C., so that not only the stems but also the wood grating is covered. The temperature of the water sinks by this operation to 25°. After a short time fermentation sets in, gases are evolved, and the liquid smells slightly of sulphuretted hydrogen. When this is observed, the water is renewed by opening the cock of a water-pipe underneath the false bottom. From this pipe branches another, opening just at the surface of the liquid, which serves to drive the scum collecting on the surface into an outlet pipe placed opposite it. In this way a stream of lukewarm water is made to flow regularly through the vat, regulating the fermentation, and at the same time carrying away all soluble substances and those rendered soluble during fermentation. After a period of from 72 to 96 hours, according as soft or hard water has been used, the retting is complete, which is easily seen when upon crushing the stem the bast separates from the woody tissue beneath.

The vat is then emptied by means of an outlet pipe at the bottom, and the wet flax placed in a machine, consisting of two pairs of rollers, in order to press out from it the remainder of the retting water. When the flax has passed the first pair of rollers, it is washed with water to remove impurities, and it is then passed through the second pair of rollers which squeeze out the greater part of the absorbed water.

When the weather is suitable, the drying of the flax is carried out in the open air, the stems being fastened between wooden clasps and hung up in an airy shed. In winter time and during damp weather drying sheds, specially heated and ventilated, are necessary. After drying, the flax is stored up from two to three months, and the straw passed through a crushing machine consisting of five pairs of rollers, each crushing finer than the last, whereby the brittle and woody covering of the stems is broken, and this is then removed by a scutching machine. The flax now only requires passing through a heckling machine in order to fit it for the market.

This method of preparing flax avoids all the evils attending the ordinary process, and, besides this, the process admits of being watched and regulated, so that a product is obtained of better quality than that got by the old retting method.

WOOD.

The tissue of the different kinds of wood employed in the arts and industries consists essentially of cellulose impregnated with incrusting matters, such as resin and similar substances, and contains also various nitrogenous and non-nitrogenous substances, various fats, oils, colouring substances, and ash constituents.

The substances penetrating and incrusting the cell membranes of the tissues are hard and brittle; their amount varies in the individual kinds of wood, being more abundant in heart than in sap wood, and in the hard and heavy kinds of wood than in the soft and light varieties. They are richer in carbon than cellulose. The greater percentage of carbon and hydrogen in wood as compared with cellulose depends upon the presence in it of the incrusting substance. According to Payen's researches, however, it is not a simple substance, but a mixture of different substances, which penetrate the cellulose in different proportions according to the variety of wood and the rapidity of its growth.

Upon the proportion of incrusting material in wood depends its density, hardness and capacity for receiving a polish. Incrusting material increases the value of wood as fuel by reason of the hydrogen it contains. The richer the various kinds of wood are in incrusting material, the more acetic acid do they yield upon dry distillation. Thus Payen operating under nearly the same conditions obtained from different materials the following amounts of pure acetic acid:—

Oak wood	4·0 per cent.
Poplar wood	3·6 „
Cotton	2·7 „
Starch	2·3 „

Wood containing 25 per cent. of water, when submitted to dry distillation, yields on the average 28 per cent. of carbon, 23 per cent. of pyroligneous acid and tar, and 39 per cent. of gaseous products. The maximum quantity of pure acetic acid obtained is 5 per cent., but the yield seldom exceeds 3 per cent.

In determining the density of the different kinds of wood it is important to distinguish between the real and apparent specific gravity. In a dry state, all the tissues of wood as well as the inner parts of the cells are filled with air. If therefore a given volume of wood be weighed in air or in water without previously expelling the air from the tissues and cells, an apparent or false specific gravity is obtained. Rumford found that the actual specific gravity of wood is always greater than that of water, and that the difference in specific gravity between the different kinds of wood is very slight, being generally between 1·462 and 1·534. For ordinary purposes, however, the knowledge of the actual specific gravity of wood is of but slight moment; the apparent specific gravity or the weight of a definite volume of dry wood weighed in the air is far more important. But, even in regard to this character, only approximate data can be obtained, and the same kind of wood has a different density according to the nature of the soil upon which it is grown, the conditions of culture, climate, etc.; as will be seen from the following table:—

Kind of wood	Specific gravity
Ebony	1·300–1·400
Oak (60 years old, heart wood)	1·170
Nut (heart)	1·000
Ro e wood	0·800
Oak (Quercus pedunculata) heart	0·850–0·800
„ „ sap	0·700–0·640
Oak (heart)	0·790
„ (sap)	0·600
Acacia	0·700–0·720
Beech and larch	0·750–0·800
Scotch fir	0·600–0·650
Small beech	0·720–0·750
Fir	0·490–0·495
Willow	0·492
Poplar	0·400–0·550
Paulownia imperialis	0·380

A cubic centimetre of the dry wood of 60 years' old oak weighs therefore 1·170 grams, a cubic decimetre 1·170 kilos, and a cubic metre 1170 kilos.

Composition.—Trunk wood when burnt yields 0·5–0·9 per cent. of its weight of ash; the bark and twigs are far richer in ash, sometimes yielding 2·5 to 3·0 per cent. The nitrogenous constitutents of trunk wood seldom exceed 0·5 to 1 per cent. The amounts of carbon, hydrogen and oxygen in a few different kinds of wood, as compared with pure cellulose, after deduction of the ash and nitrogenous constituents, are given in the following table. The fourth column of the table contains the excess of hydrogen, *i.e.* the amount of hydrogen which remains as difference if the total amount of the oxygen present be considered as combined with hydrogen in the form

of water. The last column of the table gives the carbon equivalents of wood; these data are calculated under the assumption that the excess of hydrogen has three times as great heating value as an equal quantity of carbon; they are thus found by multiplying the excess of hydrogen by three, and adding the result to the actual percentage of carbon.

	Carbon	Hydrogen	Oxygen	Excess of Hydrogen	Carbon Equivalents
Prunus Mahaleb wood	53·20	6·07	41·03	0·950	55·15
Ebony wood	52·87	6·00	41·15	0·886	55·43
Fir wood	51·79	6·28	41·93	1·038	54·90
Oak wood	50·00	6·20	43·80	0·630	51·39
Beech wood	49·25	6·40	44·65	0·720	51·41
Poplar wood	48·00	6·00	46·00	0·025	48·75
Cellulose	44·44	6·17	49·39	0·000	44·44

By treating wood successively with the following solvents—dilute hydrochloric acid, dilute and concentrated ammonia, alcohol, carbon bisulphide, concentrated acetic acid, and ammonium cuprate—a number of different substances are extracted, the nature and properties of which are still little known.

Ammonium cuprate dissolves, together with cellulose, a number of compounds which are not precipitated upon neutralising the solution with an acid, and a residue finally remains which resists all the above solvents.

The results of a few researches of this kind made with different kinds of wood are given in the following table, from which it may be seen that the individual constituents of wood occur in very different amount in the different kinds of wood :—

	Oak		Nettle Tree (Celtis Australis)	Willow
	Heartwood	Sap wood		
Water escaping at 100°	9·87	9·80	10·60	9·26
Water chemically combined	10·60	4·29	7·85	4·39
Substances soluble in the following menstrua :				
In hydrochloric acid 1 per cent.	4·55	5·53	4·75	5·71
In ammonia 5 per cent.	5·20	5·20	5·84	6·32
In a saturated solution of ammonia	8·72	6·00	6·38	6 22
In alcohol	0·50	0·45	1·76	0·35
In carbon bisulphide	0·65	0·38	0·95	0·07
In glacial acetic acid	3·90	3·28	2·67	3·68
In ammonium cuprate	25·52	37·00	36·65	34·80
Insoluble substances	23·15	28·00	14·15	22·50
Substances dissolved by ammonium cuprate and not reprecipitable by acids Loss	7·34	7·98	5·70	8·40
	100	100	100	100

The insoluble residue contains some of the incrusting material of the cellulose, together with various other substances, most of which dissolve in hot potash. Hence woody fibre is far from being a simple organic substance, but is on the contrary a mixture of a number of different substances.

Payen found in the incrusting material four substances, which, according to their solubility, he termed respectively lignose, lignin, lignon, and lignireose. The behaviour of these substances towards different solvents is as follows :—

	Menstrua in which the substances are soluble.				Menstrua in which the substances are insoluble			
Lignose	potash	soda	—	—	water	alcohol	ether	ammonia
Lignon	potash	soda	ammonia	—	water	alcohol	ether	—
Lignin	potash	soda	ammonia	alcohol	water	—	ether	—
Lignireose	potash	soda	ammonia	alcohol and ether	water	—	—	—
Cellulose	—	—	—	—	water	alcohol	ether	ammonia

Of these five substances, at present cellulose alone has been obtained in a pure state; concerning the nature and properties of the other four bodies scarcely anything is known. These substances have been submitted to elementary analysis, the results of which, however, are of no importance, since the analysed bodies may have been mixtures.

Payen examined well-washed beech wood, and found it to have the following proximate percentage composition:—

Cellulose	40
Incrusting material	60

According to Payen the incrusting material consisted of:—

Lignose	25·2
Lignon	10·8
Lignin	21·6
Lignireose	2·4

The percentage composition of these several constituents was:—

	Carbon	Hydrogen	Oxygen
For wood	50·00	6·19	43·31
„ cellulose	44·44	6·18	40·38
„ incrusting matter	54·73	6·20	40·06
„ lignose	56·10	6·09	47·81
„ lignon	50·10	5·93	44·08
„ lignin	62·25	5·93	31·82
„ lignireose	67·91	6·89	25·20

Uses.—The applications of the different kinds of wood depend upon special qualities, according to which they admit of being arranged in five groups: 1. white soft wood; 2. heavy and hard wood; 3. half hard wood; 4. coloured wood; 5. resinous and scented wood.

Poplar wood, one of the lightest of all the varieties of wood, is cut into boards for making boxes, casks, etc., and the chief result aimed at is to increase the weight of the articles packed in them as little as possible. Many manufacturers prepare from poplar wood the little boxes for packing lucifer matches. Poplar wood torn into fibres is also mixed with rag pulp in the manufacture of paper. For use as fuel poplar is one of the worst kinds of wood, since a given volume of it develops very much less heat than a corresponding volume of any other kind. The wood of the birch is much more valuable as fuel; it has a far denser tissue, and it contains in the epidermal layers of the bark a white resinous substance which protects bark and wood, and gives the wood a great heating power. The epidermal layers of the birch bark are used for making snuff-boxes and band-boxes; they resist friction and moisture better than the same material from poplar. In Canada canoes and boats are built of birch bark. Besides these applications, birch bark yields upon distillation an oil known as birch tar oil, which is used for imparting to Russian leather its agreeable smell. The lighter kinds of wood, poplar, alder, willow, lime, etc., yield upon carbonisation the charcoal for gunpowder manufactories. A recent use of poplar and fir woods is in the manufacture of spirit and paper.

The hard woods which are used as fuel and for other industrial purposes are very numerous; among those growing in this country, oak, beech, elm, ash, and chestnut are the chief. The wood of the acacia is very much prized; it is remarkable for its great hardness and tenacity, which is the result of the cells of the woody fibre being closely packed; the cell membranes are little penetrated with incrusting matter. Owing to the rapid growth of the tree, the wood is comparatively cheap to produce, at least cheaper than other kinds of wood. In acacia, the sap wood is not very thick; the amount of heart wood is on the other hand very considerable. Acacia wood, owing to its hardness and capacity of resistance, is used with advantage in the construction of various parts of machinery, *i.e.* for the teeth of mill wheels, for spinning machines, wheel spokes, and many other purposes. It has proved especially suitable for planking corridors and galleries in mines; it has been found to be from two to three times as durable as oak, and from four to six times as durable as other kinds of wood.

The innumerable applications of the different kinds of wood are too well known to need recapitulation here.

Preservation of Wood.—The preservation of wood is unquestionably one of the most important problems of applied chemistry. Owing to the enormous development

of industry, and the extension of railways, the consumption of wood increases from year to year, while its production not only does not increase, but is in many countries absolutely on the decline.

In 1791, the forests in France belonging to the State and private individuals, covered a space of 23,497,800 acres, while in 1851 they covered only 21,894,000 acres, thus showing a decrease of 1,603,800 acres during the 60 years. The condition of forests in 1851 was shown to be as follows:—

14,231,100	acres	private property
4,633,325	„	public forests
3,029,395	„	state forests.

Of late the replanting of barren tracts has been extensively carried out, in the Gascoigne especially, large districts have been planted with useful trees.

From an industrial point of view, as well as a matter of national economy, it is therefore of great importance to render timber more durable and less susceptible of decay. Formerly, only oak wood could be used for the sleepers of railways, while now, by means of an artificial hardening process, many other kinds of wood can be used for this purpose.

The chief cause of the destruction of wood is rotting or decay, which is brought about by the presence of nitrogenous substances, from which no kind of wood is altogether free. Under the influence of moisture and oxygen these substances decompose, and induce the decomposition of the more difficultly decomposable non-nitrogenous bodies, such as cellulose, etc. Moreover, the nitrogenous constituents of wood nourish fungi of all kinds, which by penetrating further into the substance of the wood promote its destruction. The greater the amounts of nitrogenous substances in wood, the more perishable it is. For this reason, wood to be durable should be felled in late autumn or in winter, but never in spring, when it is filled with ascending sap.

Many substances, very different in their nature, preserve the nitrogenous constituents of plants and animals. Among them are tannin, creasote, arsenic, pyroligneous acid, lime, salt, blue vitriol, iron dissolved in pyroligneous acid, corrosive sublimate, etc. Tannin has been employed for ages to preserve the nitrogenous matter of skins, resins and oils for embalming corpses, impregnating wood, etc.; creasote for rapidly curing meat, etc.; and salt for the same purpose. Timber impregnated with salt in the salt works of Hallein before the Christian era, has been preserved up to the present time. Aqueous or alcoholic solutions of corrosive sublimate are used for preserving anatomical and botanical specimens. All such substances as are suited for the preservation of animal products may also be used with equal efficiency for preserving those of vegetable origin.

The only difficulty met with in preserving wood by impregnation is that it is not easy to force the antiseptic solutions into the individual cells, tissues and vessels of the wood; the desired effect can only then be expected when the protective reagents actually come into contact with the substances they are to preserve. Many endeavours have been made, and with varying success, to overcome these difficulties.

Besides those methods of preservation, which are founded upon the impregnation of wood with antiseptics, it is also possible by various other means to protect wood from rotting, as by charring, baking, or smoking.

One of the oldest attempts to preserve wood is that carried out by Champy in the year 1813. The object was to preserve from rot the inner woodwork of a very moist powder magazine, the walls of which were to be covered with lead. For this purpose, the wood was soaked for several hours in a tallow bath at a temperature of from 120° to 130°. The water contained in the wood was thus expelled as steam, the melted fat taking its place. The wood took up about one fifth part of its weight of fat.

Many liquids, the boiling point of which is higher than that of water, can in like manner be employed for impregnating wood—such are oil, resins, tar, etc. By such treatment the softer kinds of wood, such as pine, Scotch fir, poplar, etc., or even denser kinds like beech, etc., can be easily impregnated with these substances. By raising the temperature to 180°, Payen succeeded in giving soft kinds of wood such durability, that they could be used in the construction of chemical manufactories, where they were exposed, not only to the action of air and moisture, but also to the influence of acid vapours and gases. It was proved that such wood suffered less than the most durable kinds of wood in a natural condition.

When timber is merely immersed for some time in the antiseptic liquid, the results produced are not very satisfactory, because the penetration of the liquid is prevented by the air in the tissues. Better results are obtained by plunging the wood entirely into the liquid in a vertical position, so that, owing to the capillary attraction

of the hollow spaces in the tissues, and partly also to atmospheric pressure, the liquid is forced into the pores and expels the air, which escapes at the upper end of the vessels.

Kyan employed in this way a solution of corrosive sublimate of 1 per cent. strength; the penetration of the liquid was assisted by having the trunks cut into boards, and after they had remained 14 days in the liquid, they were again fastened together by means of bolts.

Bréant constructed an apparatus by means of which he exposed the immersed wood to a pressure of 10 atmospheres; and the consequent compression of the air permitted the penetration of the liquid. His process was rendered still more effective by first creating a vacuum in his apparatus, so that the air contained in the tissues of the wood escaped, and it was then easy under a pressure of 10 atmospheres to force the antiseptic liquid into all the cavities of the wood.

The first industrial application of this method of Bréant's was made by Bethel, whose apparatus consists of a cylinder of sheet iron, closed in at one end like an ordinary steam boiler, and at the other end furnished with an air-tight cover secured by means of bolts. The wood to be impregnated is laid upon small trucks which are run into the cylinder upon rails laid upon the inside. According to the length of the pieces of timber, 2, 3, or 6 trucks are pushed in, the cylinder is then closed in front, and steam passed into it to expel the air; the cylinder is then cooled by allowing cold water to flow over it. The condensation of the steam causes a partial vacuum which facilitates the expulsion of the air from the tissues of the wood. After a short time a cock is opened through which the antiseptic liquid is sucked into the cylinder, then a force pump is set in action which completely fills the cylinder with the liquid, and the pump is kept going until a pressure of 10 atmospheres is attained. After several hours, according to the kinds of wood, the penetration is complete, often to the innermost core of the wood. The liquid is then run off, and the trucks containing the wood are drawn out of the cylinder, which is then ready for a second charge.

The antiseptic employed by Bethel is a mixture of hydrocarbons obtained by the distillation of coal tar. This oil of tar, wrongly termed creasote, is very suitable for impregnating railway sleepers, but is not applicable for the preservation of wood for other purposes, owing to its unpleasant smell and its inflammability. In Moll's process the wood is exposed first of all to steam in a closed chamber, then creasote vapour is admitted, which penetrates the wood, and condenses in it upon cooling. A solution of cupric sulphate is sometimes used in place of creasote.

The injecting cylinder used in this case is made of copper plates strong enough to resist a pressure of 12 or 15 atmospheres. The steam does not, as in the old method, serve to create a vacuum, but to heat the wood, enlarge its pores and destroy the ferments present in it. The copper solution is heated up to 70° before being admitted into the cylinder, in order to avoid condensation of the steam either in the cylinder or in the pores of the wood, and also the contraction of the pores that had been previously expanded by the action of the steam. The excess of steam after it has effected the expansion of the pores of the wood in the cylinder is passed through a serpentine tube and serves to heat the solution of cupric sulphate; the condensed water serves to feed the boiler and to prepare the copper sulphate solution. The rarefaction of the air within the cylinder is effected by means of a special condenser, in which the vapours are condensed; in this way it is possible not only to get rid of the steam, but of the greater portion of the air and non-condensible gases, without any serious cooling of the wood taking place, so that a condensation of the steam in the pores of the wood is prevented. The vacuum is kept up by means of air pumps which continually remove the condensed water, and work so that a barometer connected with the cylinder only shows a column of mercury 5 or 10 c.m. Finally the impregnating liquid is forced into the cylinder by the aid of special pumps, and according to the kind and size of the logs of wood a pressure of 12 or 15 atmospheres is produced.

This process is now so perfected that each apparatus is capable of receiving 10 or 12 charges per diem; and has been very extensively used in the impregnation of the sleepers of the Paris, Lyons and Mediterranean railway.

The exterior view of the entire apparatus is shown in fig. 431. The cylinder consists of copper sheets rivetted together. The lid E is rivetted on the cylinder, and the opposite lid E′ turns on an iron hinge. This lid is furnished with a wide rim that rests against a corresponding rim round the cylinder, to which it is screwed with bolts. A special adjusting screw regulates the lid in such a way that the perforations of both rims exactly fit together, and by its means the lid may be brought into the proper position, should it get displaced by any accident. A couple of levers furnished with balance weights (F F, figs. 432 and 433) are attached to the moveable axis of

the lid to facilitate the opening and shutting, so that the operation may be performed by a single man.

The closing of the cylinder is secured by laying a broad piece of rope saturated with fat upon each of the protruding rims, which upon screwing in the bolts are so pressed together that a close joint is secured. The details of this arrangement are represented by figs. 432, 433, and 434.

Besides the water and pressure gauges and safety valves, the cylinder is furnished with a number of different cocks with their connecting pipes; these are—the air cock; a cock (H) in the pipe for conveying steam; a delivery pipe for the impregnating liquid; another communicating with the condenser of the air pump; and a valve (K) for admitting the liquid into the exhausted cylinder.

The copper coil H′ corresponds with the steam outlet cock; it lies within the basin and serves for heating the copper solution. The non-condensed steam and water of

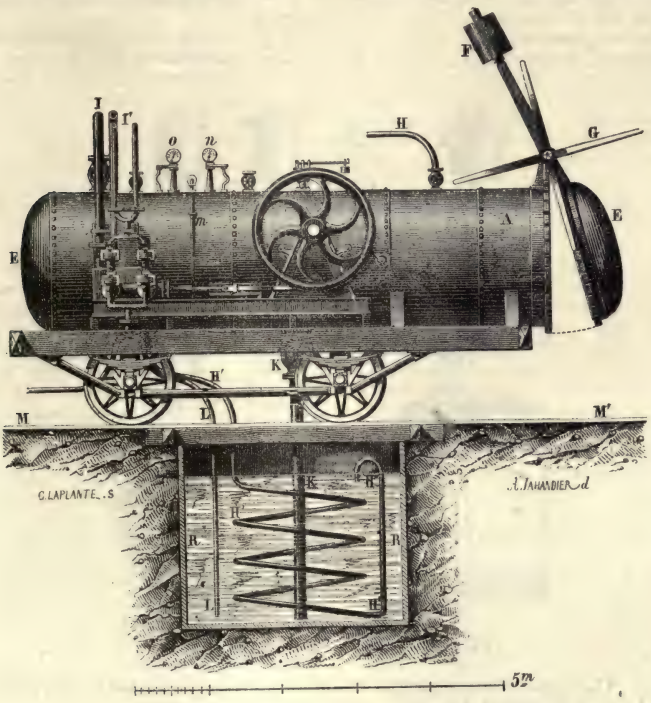


Fig. 431.

condensation are conducted into a vessel in which is contained the water for feeding the boiler, and both may be passed by means of the vertical tube H″, bent at its upper end, into the dissolving basin. The entire apparatus, with the exception of the reservoir for the copper solution, is supported upon a strong railway truck, so that it admits of being moved at pleasure. The method of carrying out the operation is as follows.

The trucks, laden with the sleepers and other pieces of timber to be impregnated, which are made fast to the trucks by means of a couple of bronze bands turning on hinges, are pushed into the cylinder. The lid which swings readily on its axis is let down and screwed on the cylinder. Directly this is done the cock, which connects the cylinder with the steam boiler by means of the tube H, is opened, the steam expels the air from the cylinder through a special cock and fills the cylinder completely, the excess of steam escaping as soon as the air cock is shut through the serpentine tube, or, provided the copper solution is hot enough, into a reservoir for feeding the boilers.

The steam pressure is generally kept up for 15 minutes; but, according to the size and kind of wood, it is often necessary to keep up the action of the steam longer, until

the innermost parts of the wood have attained a temperature of 65° or 70°. The steam is then shut off and the cylinder connected with the condenser, into which a jet of cold water is immediately pumped. At the same time the air pump is set in motion in order to remove the water pumped in, the non-condensed steam and the air escaping from the pores of the wood. Owing to the continual evaporation of water from the pores of the wood, it is not possible to obtain a perfect vacuum; the air pump is therefore kept going until the barometric column stands at 6 c.m., and the vacuum is kept up generally 15 minutes, or in the case of dense kinds of wood 25 minutes.

The large cock (K) is then opened, which places the cylinder in communication with the basin containing the copper solution. The solution has a concentration of 2 per cent. and is in the meantime heated by the escaping steam to 70°. The atmospheric pressure forces the liquid into the cylinder which fills itself nine-tenths full. The pressure pumps are then set going, to fill the cylinder entirely with the warm copper solution, and are kept going until a pressure is obtained in the cylinder of 12 atmospheres, which is maintained from 20 to 30 minutes.

The comparatively small quantity of air left in the pores of the wood after steam and vacuum have done their work is by this latter operation reduced to a very small

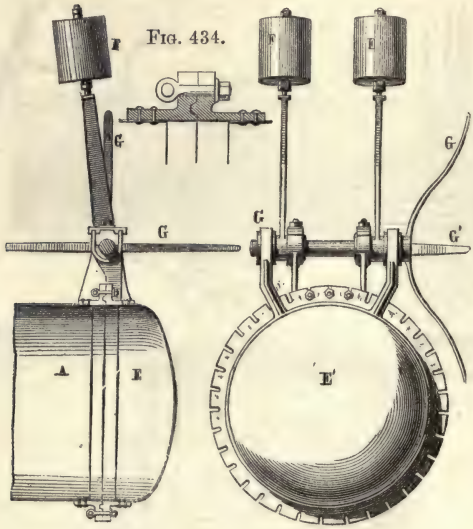


FIG. 432. FIG. 433.

volume. The copper solution occupies the space previously occupied by air, penetrates the wood, and fills up all its pores.

When the full pressure has been attained, and it has been kept up long enough, the large outlet cock is opened and the excess of impregnating liquid is run off into the reservoir. The cylinder is now opened, and both the cars are run on to a truck placed at the mouth of the cylinder to receive them. The cylinder is then charged with two fresh cars laden with timber. Each car holds 32 railway sleepers or a corresponding quantity of other timber; therefore 64 sleepers are impregnated in a single operation; and since 8 operations are carried out every 12 hours, it is possible, by working a double apparatus, to impregnate 1,024 sleepers daily.

The relative volume of preservative liquid which penetrates the wood differs according to the constitution of the wood, inasmuch as light spongy wood absorbs more liquid than dense and hard kinds of wood; and in preserving timber by this means attention must be paid to this fact. The action of the impregnating liquid is regulated accordingly, being allowed to operate for a longer or shorter time, and its strength is also modified according to the kind of wood. Dense heavy kinds of wood require a liquid of 2 per cent. strength, while for lighter sorts of wood a liquid of 1 per cent. strength suffices. Long experience has shown that wood is sufficiently impregnated when 1 cubic yard has absorbed 9 lbs. 5 oz. to 9 lbs. 10 oz. of copper sulphate.

The results of some experiments conducted by MM. Hennezel and Vétillard showed that a copper sulphate solution of 2 per cent. original strength, after removal from the

cylinder, had still a concentration of 1·728 per cent.; and the amount of liquid absorbed by different kinds of wood was as follows:

	Original weight per cubic yard	Liquid absorbed per cubic yard	Copper Sulphate absorbed per cubic yard
Oak: sleepers, square and half round, planks . . .	11 cwt. 25 lbs.	6 cwt. 51½ lbs.	14½ lbs.
Deal: half round sleepers, sound timber, 6 months felled .	8 „ 95¼ „	6 „ 104 „	15½ „
Small beech-tree wood: planks, pith wood, 8–10 years felled	11 „ 8¼ „	9 „ 13½ „	20½ „
Poplar: sleepers, sound timber, 6 months felled . . .	8 „ 95¼ „	10 „ 41¼ „	20⅞ „

Seven different experiments with oak wood showed that it took up more liquid in proportion to the length of time that had elapsed since felling; for wood between 4 months and 5 years old—*i.e.*, from the time of felling—the amount of liquid absorbed per cubic yard varied between 4¾ cwts. and 8½ cwts. It is therefore evident that the age, texture, and general condition of timber have a great influence upon the amount of impregnating liquid it is capable of absorbing.

The steaming and rarefication have the effect of altering the volume of the timber, which increases in sectional area in the proportion of 100 to 104; no increase in length, however, takes place.

The penetration of cupric sulphate into the wood may be tested by making a section of one of the pieces and dropping upon it a solution of potassium ferrocyanide; the quantity of copper salt in any particular part of the wood is then approximately indicated by the degree of brown coloration. By applying this test it has been found that sap wood is the most easily impregnable, especially when the wood has been previously heated by storing; heart wood absorbs less, but sufficient for the preservation of the wood, especially as in dense kinds of wood the most decomposable parts are the most easily penetrated by the impregnating liquid.

In Germany, railway companies have employed a similar method for impregnating their sleepers, with the difference that, instead of cupric sulphate, zinc chloride is used, which is not only as effective, but considerably cheaper, and does not require the expensive copper apparatus.

Another method has been introduced by Boucherie. It consists essentially in replacing by means of hydrostatic pressure the sap of freshly-felled wood by an antiseptic liquid, which is in most cases cupric sulphate.

The time required for perfect penetration differs considerably, and is dependent upon the density of the wood, the kind of wood treated, the amount of sap in the wood, and the length and thickness of the pieces. In oak the sap wood only is penetrated, the vessels being wider than in heart wood; sap wood is, however, the part most liable to decomposition. Beech, birch, plane, elm, fir, and Scotch fir are the kinds of wood chiefly employed, as being cheap and easily impregnated; they replace oak for many purposes. The different kinds of poplar absorb the liquid, with the exception of a small portion round their axis; the trunks are often used as poles, being cut lengthways into four parts, and the part which refuses to absorb the impregnating liquid cut away with the axe.

In all kinds of wood the circulation is easier and more complete in proportion to the nearness of the operation to the time of felling. In order to avoid as far as possible loss of sap in felling, all the branches and twigs are immediately chopped off. When the felling takes place before the budding of the trees between January and April, the trunks are most fitted for impregnation in the course of a couple of months, at which time a disc about 4 inches thick is chopped off from the end of each trunk on account of these portions being too dry. In summer the impregnation ought either to be carried out at once, or at the latest within 8 or 12 days from the time of felling.

The impregnation process is also easier in proportion to the shortness of the trunks and the pressure of the liquid. The diameter is also of importance; for while a trunk 9 feet long and 15 inches in diameter is completely impregnated in 24 hours, 100 hours are required for the perfect impregnation of a trunk having the same length but a diameter of 2 feet; and besides this it is necessary to pass through it a quantity of impregnating liquid equal to six or seven times its volume. Indeed, in the case of such thick trunks, it is advisable, after the outer parts have been sufficiently impregnated, to give the interior parts a special treatment by screwing on to the trunk a board of

sufficient size, and exposing the harder parts of the tissue once more to the pressure of the liquid. The complete penetration of the harder parts is often secured by inverting the block and passing the copper solution in at the outflow end.

Above all things it is absolutely necessary that the cupric sulphate employed should be as pure as possible, and free from excess of acid; it is especially necessary that it should contain no ferrous sulphate, since this salt exerts an oxidising action upon the fibres. The absence of ferrous sulphate may be proved by a solution of cupric sulphate yielding with ammonia a blue and quite clear liquid. In order to avoid rendering the solution of cupric sulphate impure, all the vessels employed in the impregnating process are made of wood, bronze, or brass.

Cupric sulphate preserves wood by fixing itself upon the cellulose, lignin, and nitrogenous substances present in the wood. It is poisonous enough to prevent insects from lodging themselves in the tissues of the wood; besides which, owing to the displacement of the sap, a number of the most easily decomposable constituents are removed from the wood.

Recent experience has shown that a slight variation may be made with advantage in the above method of proceeding. This may be easily done by allowing the liquid to run away until the greater part of the sap has escaped; the process causes the loss of a small quantity of cupric sulphate, but a liquid of a purer quality is passed into the wood.

A method a little different to the above, and proposed by Renard-Perrin, consists in forcing the impregnation liquid into the wood by atmospheric pressure. For this purpose the logs placed in an upright position have their lower extremities connected with an iron vessel in which a vacuum has been made by burning in it balls of tow soaked in alcohol. Directly the flame has burnt out the iron vessel is closed, and upon cooling down a partial vacuum is produced within it. The impregnating liquid, which is poured upon the upper end of the wooden block, is then forced downwards through the wood by the pressure of the atmosphere. This operation several times repeated suffices for the impregnation of the wood. Perrin's method is, however, more used for preparing coloured wood than for preserving wood by antiseptic liquids.

For colouring wood in the above way a number of colours and mordants are employed, which are likewise used for dyeing cloth; thus the different shades of red and violet are obtained by using madder, alkanet, orchil, logwood, and Brazil wood; blue is got by using litmus, indigo, logwood; green by cupric acetate, or verdigris; black by using extract of oak galls, ferrous sulphate, etc. Other kinds of wood are bleached by a similar process; thus the wood of the dwarf beech is bleached by treating it with a very dilute solution of soda ($\frac{1}{4}$ per cent.), then with water, chloride of lime, dilute hydrochloric acid, and finally again with water. Wood thus bleached is used instead of ivory in mosaic work.

Timber or wood that has been impregnated is not only useful for the purposes for which up to the present it has been almost exclusively employed, such as railway works, etc.; but it may be also employed with great advantage for a number of other purposes: such as carpentry work which is exposed to the action of atmospheric air and moisture, the timbering of galleries in mines, for posts and stakes of all kinds, such as telegraph posts, and for many parts of ships, etc.

Tannin or tannic acid must be reckoned amongst the best preservative agents: it enters into combination as well with the nitrogenous constituents of wood, forming with them insoluble and difficultly decomposable products, as with the nitrogenous constituents of animal tissues, as in leather. The durability of oak wood is ascribed to the large percentage of tannin it contains, but it is very probably due still more to the great density of the tissues. Fishermen are in the habit of dipping their nets and sails from time to time in liquids containing tannin which gives them greater durability.

From the most remote times, wood tar has been used for preserving the timbers in ships, and its application at the present day for the same purpose is a sufficient proof of its usefulness as a preservative agent. The active preservative principle in wood tar is creasote; in coal tar a kindred substance is found, which is called carbolic acid.

Carbolic acid, even when present in the smallest quantity, possesses the property of checking processes of fermentation and decay, and of destroying lower organisms both vegetable and animal. Carbolic acid is obtained in large quantities as a by-product of the manufacture of gas and of paraffin oil, and being very cheap it might be used with advantage for preserving timber.

When wood is treated with oils, fats, wax, and resins in the melted state, its pores are filled with them, and it is rendered impervious to air and moisture; however, all these bodies are too dear to admit of general application in the preservation of wood.

Salt preserves wood just in the same way as it does meat, fish, and similar materials; in moderately moist situations, as in certain mines, timber impregnated with salt resists decomposition for a considerable length of time. Salt cannot, however, be used for this purpose in very wet places, since it would be dissolved out, nor can it be used in places where it would at one time have opportunity to absorb water, and then again to become dry, as this would cause a crystallisation of the salt between the fibres of the wood and be detrimental to its durability.

A number of iron salts have been used for preserving wood. The most useful of these is unquestionably iron acetate, obtained by dissolving iron in the impure acetic acid called pyroligneous acid, or the aqueous liquid obtained by distilling wood, which contains besides acetic acid a number of other substances, such as creasote, etc. The value of iron salts for preserving wood seems, however, very problematic. Watteau has introduced a method of treating wood with ferrous sulphate, but it is not probable that much good will be obtained from it. The timber is first impregnated with a solution of barium sulphide (5 per cent.) under a pressure of 10 atmospheres, and then in like manner with a solution of ferrous sulphate of 5 per cent. According to M. Watteau, the sulphuric acid is precipitated within the wood as barium sulphate, and ferrous sulphide is produced, an excess of barium sulphide remaining, which is poisonous to insects, cryptogams, and ferments. Barium sulphide, however, is readily decomposed, and would be converted by the air into insoluble or inactive barium carbonate, and then the ferrous sulphide would be converted by the air into sulphate, which is most of all detrimental.

Cupric sulphate and zinc sulphate act as antiseptics without exerting the injurious effects produced by the corresponding ferrous salt.

Basic lead acetate forms with the most easily decomposable constituents of wood insoluble stable compounds. It penetrates wood easily, and may be used with advantage when it can be obtained cheaply.

Mercuric chloride or corrosive sublimate has long been used for preserving anatomical and botanical preparations, and as well as arsenious acid is sometimes used for preserving wood. The use of both these substances, however, on account of their poisonous nature, has been now for the most part given up, since both by the impregnation as well as in the further working up of timber thus treated the danger to the workmen is very considerable. Wood impregnated with corrosive sublimate, and used in the building of greenhouses, was found to be injurious not only to creepers trained to the wood itself, but also to the entire vegetation in such houses.

Zinc chloride is an excellent preservative for timber, and is much employed for curing railway sleepers; but care must be taken that it contains no free hydrochloric acid.

Calcium chloride is in its action similar to common salt; it is used with advantage for the hoops of casks deposited in dry places, since owing to its hygroscopic nature, it gives the casks a certain degree of moisture and prevents their shrinking.

It has been already mentioned that the perishable nature of wood is due to the constituents of the sap, which are in themselves of a decomposable nature and impart this property to the wood itself. This tendency to decomposition is favoured by the fact that certain constitutents of the sap possess the property of absorbing moisture even from moist air. Neither fermentation nor decomposition can take place in the absence of water, and hence many methods are employed either to alter the nature of the constitutents of the sap, and render them less hygroscopic by baking, surface charring, or smoking, or the sap constitutents are expelled as far as possible by steaming the wood.

In baking wood care must be taken to dry it well before submitting it to the baking process, otherwise the wood would crack and split. Well-dried wood is placed in a brick chamber, into which a stream of hot air is forced by means of a blast The air is heated by forcing it through a fire, the gaseous products of combustion being then passed into the drying chamber, so that the effect of smoking is connected with that of baking. Care has to be taken by means of proper regulation of the heat and by ventilation that the temperature of the wood is raised very gradually, otherwise it is certain to crack, and that no sparks from the fire are carried into the drying chamber.

Baking causes wood to shrink, the tissues become denser, the juices are altered in composition, and the wood is rendered more durable. To obtain good results, the temperature must be finally raised so high that the surface of the wood appears of a yellow or brownish hue.

The steaming of wood is carried out in the way already mentioned in treating of the impregnation of wood; when however steaming is the only preservative employed, it requires to be continued for a longer time. Steam either under high or ordinary pressure is made to act upon the wood until the condensed water runs off colourless,

or until it ceases to extract colouring matters. According to Prechtl it is well to cause vapour of tar to act upon the wood together with steam, which is effected by placing a small quantity of tar in the boiler as soon as the condensed water from the wood runs off colourless; the tar vapour passing over with the steam penetrating the wood and giving it greater durability. Steamed wood dries well without distortion or cracking; before drying it is soft and pliable, and may be bent into any desired shape. This property of steamed wood is taken advantage of in bending the staves of casks and the fellies of wheels, etc. After cooling and drying, such wood assumes its original hardness.

According to a process introduced by Chemallé, wooden bolts and wedges are rendered very hard and durable by steaming and smoking. They are first steamed and then soaked in a bath of hot oil or coal tar; while still hot they are submitted to strong pressure in a specially constructed machine, and thus reduced 20 per cent. in volume. A machine of the kind made by Ransome and May in Ipswich produces 18,000 finished bolts every 10 hours.

Surface charring has been long employed for preserving wood. Posts that are to be placed in the earth are previously burnt at their lower extremities, by which means the essential aim of baking is attained. A century ago a trial of this method was made for preserving the keels of ships; the result was favourable, but the process was not further carried out, probably on account of fire risks.

A gas flame is made to play upon the part of the ship to be charred. The gas is contained in wrought-iron cylinders filled at the gasworks under a pressure of 11 atmospheres. Under the ordinary pressure of the atmosphere each cylinder holds 26·487 cubic feet of gas. The cylinders are brought from the gasworks to the ship yards on cars, and are there connected with a regulator, which admits of the gas escaping from them under a pressure of about one inch of water. The gas is conducted by means of india-rubber tubes from the cylinders to the burners, which are connected with a blast, by which a large and hot flame is forced against the part of the ship that is to be charred. One square yard of surface requires 5·88 cubic feet of gas.

The same process has been employed with success by Lapparent for disinfecting the interior of ships. The methods formerly considered sufficient, such as thorough washing and disinfection with chlorine, or painting over with chloride of lime, have all been found to be comparatively inefficient.

The charring of the interior of ships causes a quick evaporation of the absorbed moisture, when a torrification of decomposable substances or spores and germs of plants and animals, and finally a partial dry distillation of the wood, by which it becomes charged with pyroligneous acid, creasote, hydrocarbons and other antiseptic substances.

The apparatus employed is the same as that used in charring the exterior of ships. A couple of workmen are required, the one to regulate the flame and the other the blast; they can easily char 12 sq. yards in 10 hours, using 5·88 cubic feet of gas per square yard. Not only are the wooden parts of ships thus treated, but the iron heads and bolts and other iron portions of the vessels are also submitted to the same operation, the rusted surface of which is especially suited for harbouring spores and germs. The unequal expansion of the metal and of the rust attached to it causes the latter to fall off in large pieces.

Iron ships are also treated in like manner; the greater capacity of the metal for conducting heat requires, however, a stronger blast and greater consumption of gas than is required in treating wooden vessels. Experiments made at Woolwich showed that iron ships require a consumption of gas equal to 7·35 cubic feet per square yard.

Since the use of illuminating gas would for many purposes be too expensive, it has been replaced by oils, the heavy hydrocarbons obtained from coal tar; common kinds of fuel, coal, and even coke, is burnt in a specially constructed apparatus in such a way that a lengthened flame is obtained. This kind of apparatus is used for the surface charring of railway sleepers, telegraph posts, etc.

The heavy hydrocarbons have been employed by Lapparent. These oils can be used with advantage for charring wood, since the smoke they produce does not interfere with their application, and by means of suitable apparatus the smoke may also be burnt and used as fuel.

For this purpose Lapparent constructed a lamp of peculiar construction, the chief feature of which is a large cylindrical hollow wire, through which air is passed by means of a concentric tube and a blast. The oxygen of the air effects the complete combustion of the carbon of the hydrocarbons, so that a large and almost smokeless flame of a very high temperature is produced which is made to play upon the surface to be charred. When stakes and such articles are treated, the lower ends are placed

directly in the flame a little further than they require to be buried in the earth ; larger objects, such as rafters, sleepers, etc. are supported upon bearers, so that they can easily be turned. Comparatively rough timber work can be thus treated, and even finished carpentry work admits of being rendered hard and durable by this means ; if such work requires painting, all that is necessary is to scrape off the charred surface.

The combustion of the oil of tar is facilitated and rendered more equal by mixing it with an equal volume of heavy petroleum, which does not ignite spontaneously upon dipping into it a burning splint.

An apparatus for charring railway sleepers, etc. constructed by Hugon, is represented in front view by fig. 435, and in end view by fig. 436.

It consists of a cast-iron cylinder (A), furnished above with a tube (A′), which serves for the introduction of the fuel. At the other end of the cylinder is an opening shown in the figure closed with a lid and screw for drawing out the ash. The flame and combustible gas escape at the mouth of a tube 2 inches wide, at the upper part of the cylinder ; opposite the ash door there is a horizontal tube connected with a blowing machine by means of a caoutchouc tube. A small tube (*f*) is inserted into

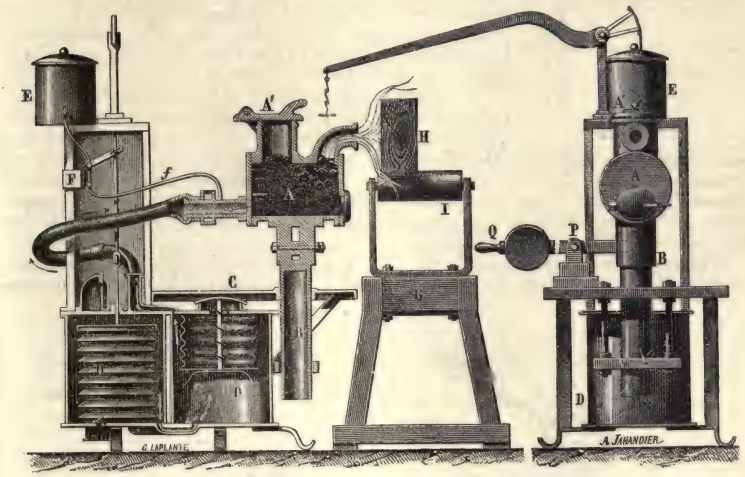


Fig. 435. Fig. 436.

this blast tube and serves for injecting a fine stream of water into the red-hot fuel. This is effected by causing the lever which moves the blast to press upon a piston in the water tank (E), so that in proportion to the action of the blast the required quantity of water is injected into the fire. The furnace (A) is supported by the cylinder (B), moveable upon its axis, by the means of the lever (P) and the weight (Q), so as to admit of the entire furnace being raised or lowered to give the flame any desired direction. The blowing apparatus (D) is furnished with air chambers by means of which a uniform blast may be produced.

To set this apparatus going, small pieces of wood are thrown into the furnace (A) through the ash hole ; this is ignited and the furnace is half filled through the opening (A′); all the openings remain open, the draught then effecting combustion ; both openings are then closed and the blast set going. The air passing over the ignited fuel accelerates the combustion and causes a strong flame to issue from the exit tube. When the volatile portions of the coal are destroyed, the residue remaining in the cylinder consists of coke, which burns almost without flame. At this point the piston of the water tank is connected with the connecting rod of the blast, and the cock (F) opened so as to inject a fine stream of water upon the coke. The water is at once converted into vapour and decomposed by the red-hot coke into hydrogen and carbonic dioxide, which in contact with the red-hot coke takes up carbon and forms carbonic oxide. A combustible gas is thus obtained which issues from the exit tube and burns with a long and intense flame. It is true that the conversion of carbon into carbonic oxide does not effect the most economical use of combustion heat of coke, but the object in view is attained, viz. the production of a flame large enough to cover the surface to be charred. The sleepers (H) to be charred rest upon metal rollers (I) supported by the frame (G). The rollers are set at a distance of 6 inches

from the burner of the furnace. The sleepers are exposed to the action long enough to char the surface as required, by pushing them slowly or quickly along the rollers. By raising or lowering the furnace the workman is able to guide the flame directly upon the wood, so as to economise the heat.

In charring cylindrical stakes, such as telegraph posts, the apparatus represented by fig. 437 may be conveniently employed. It is fastened at C to the support (G fig. 435), and consists of an iron pillar turning upon the point (O), the upper part of which is furnished with a piece of sheet iron bent so as to form a gutter. The portion of the stake or part to be charred is laid in this gutter, the flame made to play upon it and the gutter moved slowly forwards. The flame bends itself in the shape of the gutter, thus playing completely round the stake or post, charring it equally, without it being necessary to give it a rotatory motion. The end of the post which is to be placed in the earth requires more complete charring, for which purpose it is again exposed to the action of the flame after the whole post has been charred; this is done by turning the whole apparatus at a right angle round O, by means of the lever (N), so that the entire end of the post is exposed to the full action of the flame.

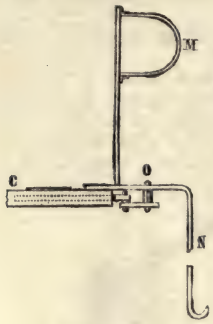


FIG. 437.

In mining and excavations for railway works, etc., rocks are often met with which are so hard that boring is very expensive, and blasting effects only the loosening of small pieces. In such cases the cohesion of the rock may be considerably loosened by means of heat. This fact was known and employed ages ago, but has been almost neglected on account of the imperfectness of the old method. More recently the application for this purpose of an apparatus similar to that described for charring timber has been employed with great success.

The apparatus is represented by fig. 438. It consists of a furnace (A), the fore part of which is turned towards the part of the rock to be heated, and in front of the open-

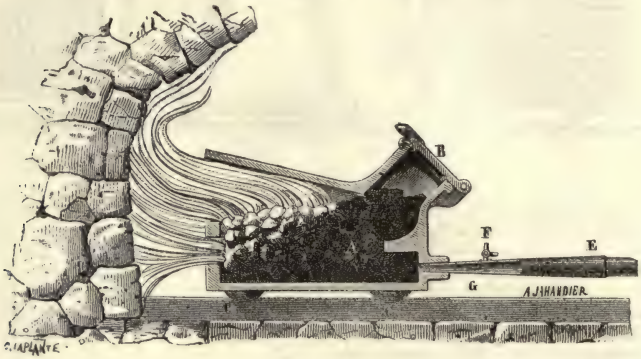


FIG. 438.

ing is placed a cross bar to prevent the coal falling out. The furnace itself runs on four wheels upon a tramway. A lever (E) at the hinder part of the furnace serves for giving it an inclined position, so as to direct the flame upwards if necessary. The hinder part is also furnished with a blast nozzle connected by means of tubing with a blowing apparatus.

Dry wood is ignited in the furnace, air being allowed to enter very slowly, and coal is then thrown in through the opening (B); when the first portions of coal are ignited, fresh coal is added until the furnace is completely full. After about 15 or 20 minutes, when the coal is quite red hot, the mouth of the furnace is placed against the rock to be loosened, and air is forced in. The air, as in the apparatus above described, conducts water to the fire, which drops through the cock (F) into the blast nozzle; this causes a large flame to issue from the mouth of the furnace, and play over the surface of the rock, heating it so considerably that, in consequence of unequal expansion, in the course of a short time pieces of rock loosen and fall away. When the

rock is very hard, it often happens that pieces of rock are ejected with sufficient violence to cause injury to the workmen.

So soon as the work begins to split and show cracks, the furnace is removed to another spot and the flame made to play upon new portions of rock. The heated rock is then chilled with cold water, and can be easily removed.

For loosening rocks which offer difficulties in blasting, this apparatus is three or four times as effective as blasting powder. It is only necessary to adapt the dimension of the furnace to the hardness of the rock, the size of the surface to be loosened, etc. In experiments made at Echallange, with quartz rock containing galena, there was excavated in a gallery during 54 working hours a space 5 ft. high, 4¼ ft. wide, and 6½ ft. long.

A new industry started by Latry in Grenelle has recently attained a certain importance. It consists in condensing the sawdust from rosewood, and using it for imitations of carvings in ebony, mosaic work, dice, etc. The sawdust is for this purpose carefully sifted and mixed with ¼ to ⅓ of its volume of blood, previously so far diluted with water as to admit of the entire mass of sawdust being completely moistened by it. The mixture is spread out upon hurdles, and dried in a kind of oven in a current of air of a temperature of 45°.

After cooling, a friable mass is obtained which is then worked up. For this purpose strong cast-iron boxes are employed, the bottom of which is furnished with the matrix of the object to be moulded. The matrix is then covered with the powdered mass and this stamped in under a pressure of 500 tons; the space left after removal of the pressure is filled in with more powder and then again pressed, the operation of filling and pressing being continued until the matrix is quite full. The compressed mass is then heated to 175°, by placing red-hot bolts 2½ in. thick in special apertures of the iron moulds, which communicate their temperature to the pressed powder. The high temperature and pressure is kept up, according to the size of the object to be moulded, from half an hour to an hour. The condensation is so considerable that the moulded objects acquire an apparent specific gravity of 1·300, while rosewood has a specific gravity of 0·800; their hardness is so great that they admit of being cut and polished like ebony. Wood thus prepared is extensively employed for different articles of elegant cabinet work.

The union of the wood particles is effected by the blood fibrin, softening at a temperature of 175° and hardening to a solid mass upon cooling; besides this, there is no doubt that a resinous substance which is present in large quantities has also an influence. Payen extracted from rosewood by means of alcohol 35 per cent. of a resinous substance.

PAPER.

History.—In the earliest periods of civilisation, paper was perfectly unknown. The oldest writings were not traced upon paper, but upon stone and tiles; afterwards wood, barks, leaves, and also bones, skins, metal plates, etc., were used. In the time of Alexander the Great, papyrus, prepared principally in Alexandria from a plant growing on the banks of the Nile, came into use. According to Pliny a layer of fibres was placed side by side and close together upon a board; another layer was then placed transversely over these; the whole was then moistened with water, or with a solution of sugar containing vinegar, and so pressed together by rubbing with a burnisher or beating with a hammer as to become united into one sheet. Such was the composition of the paper upon which the works of Cicero and Virgil were written.

Parchment also was in early times and is still used for writing upon. It is said to have been discovered in the third century B.C. by Eumenes, King of Pergamos. It was prepared from the skins of asses, sheep, pigs, goats, and other animals, a material that had been used before, but in a less prepared condition.

The discovery of the preparation of paper from vegetable fibre and tissue must be attributed to the Chinese, who have practised the art for two thousand years, and at the present time produce the finest varieties of paper. Their method is still nearly the same as at first, and as imperfect as that which is still current in many of our paper mills in the preparation of the so-called hand-made paper. The Chinese method of making paper was known in Persia A.D. 650, and it was introduced from there into Arabia about A.D. 700. The Arabians transplanted it into Spain, from whence it spread into France, Germany, and England. The first paper manufactories in France were established at the commencement of the fourteenth century at Troyes and Essones. In Germany, manufactories were established at Ravensburg in 1290,

Kauffbeuren in 1312, Nuremberg in 1319, and Augsburg in 1320. The English paper manufactories had their origin later, in the fifteenth or sixteenth century. In Holland the manufacture was very much perfected at a comparatively early period, and an apparatus called a hollander was invented for tearing the rags by means of cylinders having sharp ridges, instead of the previous very tedious way of disintegrating them by mallets. Paper was first dried by means of cylinders heated by steam at Crompton.

A considerable advance in the paper manufacture resulted from the discovery of the artificial preparation of soda, as well as the artificial bleaching materials, chlorine and the hypochlorites. The latest revolution in the art of paper making has been in the use of substitutes for rags, especially of wood and straw.

Composition and Properties.—Paper is to be considered as a felt-like coherent mass of fine vegetable fibres. The vegetable fibre, or its tissue as it occurs in nature, is submitted to a thorough purification to free it from foreign constituents; it is then brought to a state of fine division and stirred up with water to a paste, which is spread out over an even surface, where, upon the removal of the water, the intertwined fibres remain united into a uniformly thick solid mass. Paper made from vegetable fibre consists consequently of the purest possible cellulose.

The most essential properties of paper, by which its quality is estimated, are its firmness, smoothness and glossiness of surface, its colour, transparency and durability. Paper should offer a certain amount of resistance to tearing. For some purposes it must possess a rough surface and be opaque; for others a smooth and transparent paper is required. It is very essential for writing-paper that it should retain its colour and firmness as long as possible.

Preparation, Materials.—In the manufacture of paper, vegetable fibres are almost exclusively used, as they possess in a much higher degree than do animal fibres the property of being worked up into a closely felted sheet. These fibres occur either as the refuse of worn out tissue, as rags, or they are prepared specially for the paper manufacture, and are then called surrogate. In rags two kinds of fibre-tissue have to be dealt with, linen and cotton.

The fibres of linen are round tubes with thick walls, formed of concentric layers of cellulose. The density of these tubes increases from within, or the newer formation, to the outer or older parts. Each separate fibre is pointed at both ends, has a smooth surface, is flexible, and is so firm that it will undergo considerable pressure without being crushed or pressed flat.

Cotton fibres also are formed of small tubes, the walls of which are much thinner than those of linen. Consequently these fibres possess much less firmness, and by a slight pressure are pressed together into a sort of band. Whilst, too, the linen fibre is pointed at both ends, the cotton fibre is pointed only at one end. These two conditions cause the felting of cotton fibres to be more difficult and less close, and therefore cotton rags are not so suitable to the paper manufacture as linen rags; the latter yielding a closer and smoother paper.

Woollen and silk stuffs are not suitable for the paper manufacture. Their fibres are not hollow; they are consequently too rigid and hard. They are only used for making packing papers. In recent years the substitutes for rags have become of greater importance to the paper manufacture, and especially among these wood and straw.

The kinds of wood especially suited for the paper manufacture are those which are least compact in structure, so that they can easily be brought into a finely divided condition. They are principally light woods, such as the fir, pine, poplar, birch, lime, hornbeam, etc.

In the preparation of wood for the manufacture of paper, the individual fibres have to be isolated as much as possible, and freed from incrusting material, such as resin, albumen, tannin, oil, etc. This is effected either by mechanical or chemical methods, or by the aid of both.

Preparation of Surrogate by Mechanical Treatment.—The most remarkable mechanical method of preparing wood was introduced by Woelter, of whose machines a great number are in use in Germany, Belgium and France. By this method the wood is ground under a continuous jet of water, the wood being pressed against the grindstone parallel to the fibres or the axis of the tree. The apparatus consists of three principal parts: the defibrator, which is a grindstone of sandstone, having a surface sufficiently rough to tear and disintegrate the fibre of the wood pressed against it; the purifier, or sorting apparatus, a series of drums provided with metal sieves of various sized meshes, through which the fibres suspended in the water are deposited in different heaps; and the refiner, by which the inferior and coarser woody fragments are converted into a fine paste.

The defibrator consists of a grindstone, 4 ft. in diameter and 16 in. thick. Its axis lies horizontally in two cast-iron sockets. It makes 150 revolutions a minute, for which a driving force equal to 45 to 55 horse-power is required. A machine of 50 horse-power only yields about half a ton of marketable wood fibre daily. This considerable consumption of force in comparison with the yield limits the use of the machine to districts where there is an abundance of water power and wood. Over the grindstone are, according to its size, five or more iron chests. The wood to be disintegrated, sawn into pieces about 14 in. long, is laid in these chests with its fibres parallel to the axis of the grindstone, against which whilst rotating it is pressed by a spiral arrangement that pushes the wood forward at the rate of from 1 to 3 ft. per hour. Above the grindstone are also two cocks through which water is allowed to run in sufficient quantity to keep the rubbing surface always wet. The wood paste flows away into a reservoir placed underneath the stone.

The epurateur or sorting apparatus consists of a series of troughs each provided with a drum sieve with its axis fixed horizontally. These drums are 1 foot in diameter, $3\frac{1}{4}$ ft. in length, and are completely covered with wire gauze, each drum in succession having finer gauze than its predecessor. The wood paste from the reservoir is run through a coarse sieve, which retains the largest pieces, and then allowed to stand a short time in a settling tank, during which time especially any sand that may have been derived from the grindstone is deposited. The paste passes from here through the drum sieve of the first sorting trough. A portion of the woody fibre remains behind, but the finer fibre passes through the gauze and the hollow axis of the drum into the second trough, where another portion is retained. This is repeated until the last drum of the series is reached, through which only water should pass, the meshes being sufficiently fine to retain the finest fibre. The rate of rotation of the drums varies: the first makes 30 to 36, the second 15 to 18, the third and fourth 18 to 20, and the fifth 15 revolutions per minute. The wood fibre accumulating on the exterior is scraped off by means of a small cylinder, and thrown into a collecting vessel.

The raffineur consists of two mill-stones, the lower of which is stationary, the upper rotating upon it. Into this apparatus are placed the portions of fibre retained by the first, or first and second drums, and ground into a fine paste, which is brought again into the sorting apparatus. The loss of wood by Woelter's method amounts to 50 per cent.

The greatest difficulty in the preparation of ground wood stuff is the impossibility of bleaching it with chlorine or chloride of lime, which would colour the wood fibre yellow or brown. If on the other hand an unbleached wood fibre, perfectly white in appearance, be used, the paper prepared from it darkens very rapidly when exposed to the light. A good bleaching material for ground wood fibre has yet to be discovered. Sulphurous acid imparts to it a light yellow colour; oxalic acid, which has been recommended in several quarters, has scarcely any action.

Falkenhayn has patented in Bavaria a wood disintegrating machine, in which the wood is rasped by pressure against a cast-iron cylinder set with steel saw-like teeth. The mass, in the condition in which it comes from the cylinder, can be used as an addition to ordinary paper paste. In order to make it available for finer paper, it is passed between two spirally channelled cast-iron cylinders. By this machine half a ton of pine-wood can be disintegrated in twenty-four hours. Similar wood disintegrating machines are still constructed in great number. One that is highly spoken of was exhibited by Decker and Co. at the Paris exhibition of 1867.

The rasped wood stuff is inferior in quality to the ground, the separate fibres being so much broken up that their capability of felting is much diminished, and the paper is not so strong.

Preparation of Surrogate by Chemical Treatment.—For a long time chemical agents have been used to free the cellulose of wood, straw and many other vegetable tissues from the incrusting materials, and to prepare it in a pure condition. These methods can in some measure be made useful in the preparation of wood for the paper manufacture.

In the manufactory at Pontcharra, Messrs. Orioli, Neyret, and Frédet treat slices of wood one-fifth of an inch thick, or wood shavings, at a warm temperature with a kind of aqua regia, then in a closed double-sided vessel with ammonia or soda, and thus free the wood from the incrusting material. A subsequent bleaching process with chloride of lime, and washing, suffice to produce a beautiful white and pure wood stuff, which forms an excellent substitute for rags. The proportions for the aqua regia, according to Orioli, are one part of nitric acid to four parts of hydrochloric acid. If more hydrochloric acid be used the wood is turned brown.

In the method of treating with aqua regia in the cold, the well-dried slips of wood, one-fifth of an inch thick, are placed in a mixture of 94 parts of strong

hydrochloric acid (sp. gr. 1·160) and 6 parts of nitric acid, contained in an earthenware vessel capable of holding about 200 gallons, and left in contact with the aqua regia during six to twelve hours. The wood absorbs about 50 per cent. of its weight of the acid; the excess of acid is mixed with fresh aqua regia and used in a subsequent operation. A portion of the colouring substances is changed into picric acid; the incrusting material is partly dissolved and partly converted into a soluble condition; whilst the fibrous cell substance, with careful treatment, is not attacked.

The method of treatment with hot aqua regia is to be preferred to the foregoing, because by it the cellulose is more preserved, whilst the foreign substances are more strongly attacked. For 100 parts of wood about 260 parts of aqua regia, or sufficient to dip the whole of the wood slips in at once, are taken. The liquor consists of 6 parts of strong hydrochloric acid, 4 parts of nitric acid, and 250 parts of water. The entire operation is carried out in a wooden trough, the bottom of which consists of a granite slab cemented to the edge of the wooden trough with caoutchouc. As soon as the trough is prepared with the aqua regia and wood, steam is passed in through a wooden pipe, at the end of which is a valve to prevent the aqua regia from flowing into it.

After treatment with either cold or hot aqua regia the excess of acid is poured off, and the woody mass is washed in the same vessel several times with fresh water. The washed slips of wood are then crushed into a brown mass by means of vertically placed granite mill-stones, again washed with cold water, and finally, in order to remove the last trace of acid, treated with a small quantity of milk of lime.

In the washing with alkaline liquor there is used in the manufactory at Pontcharra an apparatus invented by Neyret, Oriolo, and Frédet. It consists of a strong rotating iron cylinder, 13 ft. 4 in. long and 6 ft. in diameter, resting on its axis in a strong iron frame. The rags or wood stuff, as well as the alkaline wash liquor, are introduced through a manhole. The cylinder is surrounded by a jacket, leaving a space into which steam can be introduced. The steam enters through the hollow axis, and a stuffing box into this space; the condensation water flows back into the steam chest through the steam pipe. In this manner the inner cylinder is heated over its entire surface. A too great loss of heat is prevented by a wooden shell covering the outside cylinder, and over this again is a thin tarred sheet-iron case. During the working the manhole of the inner cylinder is closed air-tight. A cock above is available for the recovery by distillation of ammonia when it is used; whilst a cock at the bottom of the cylinder is used for drawing off the liquor freed from ammonia, or the soda ley when soda is used.

As the operation is effected in a closed vessel, this apparatus is especially suitable for the use of ammonia water, because the vapour of this liquor, by heating, produces double the pressure of water vapour. When heated with water vapour up to 145° or 152°, the pressure in the inner cylinder produced by the ammonia vapour corresponds to eight to ten atmospheres. The revolutions number 1½ to 2 per minute; the contents of the inner cylinder amount to 2,000 gallons.

When wood stuff is to undergo treatment with alkalies in this apparatus, a quantity of about 2 cwts. is placed in the inner cylinder, 600 or 700 gallons of solution of ammonia added, to which a further addition of 50 or 60 lbs. of caustic soda, to preserve the ammonia in the caustic state, is an improvement; the manhole is closed air-tight; a tap communicating with the space between the two cylinders through which air can escape is opened; steam at 150° is admitted to the inter-space, and the apparatus is set in motion. After 5 or 6 hours the process is ended. The ammonia is then distilled off, the liquor is allowed to run away, and the apparatus is turned so that the manhole is underneath; upon the removal of the lid the wood stuff then falls out. Instead of ammonia a corresponding quantity of soda ley can be used. This is prepared direct for use by dissolving 7 parts of soda in six times its weight of water, and rendering it caustic with lime water containing 5 parts of burnt lime. The turbid liquor is allowed to stand, and the clear ley afterwards drawn off.

The bleaching of the wood stuff after treatment with alkali is effected with chloride of lime. The greatest care must, however, be used that the cell substance itself is not burnt by it. Ordinarily for 100 parts of wood paste, 50 parts of chloride of lime are taken. The total loss amounts to 60 per cent. of the weight of the wood.

The difficulty in the above-described methods consists, according to Orioli, in the large vessels used for the action of the acid mixture upon the wood. Sandstone vessels always let the acid through, and finally show cracks that cannot be sufficiently stopped up with wax. Besides, the workmen are exposed to the vapour of nitric acid, so that latterly the chemical method has been abandoned, notwithstanding that by it a very fine and useful wood stuff may be obtained.

Bachet and Machard's method of treating wood has a double object: the bringing of the wood into a fine fibrous and easily felted mass, and the conversion of the

incrusting materials into sugar. A portion of the cell fibre also is always converted into sugar, but it is exactly that portion that is most recently formed and least tough. This condition therefore is so far favourable, that the remaining fibres are tough and more easily felted. Experiments carried out in Payen's laboratory, in one of which 14 oz., and in two others 18 oz. of deal slips, $\frac{1}{2}$ in. thick, were treated for ten hours with a boiling mixture consisting of $3\frac{1}{2}$ pints of water, and $\frac{1}{3}$ pint of strong hydrochloric acid, gave on the average 21·13 parts of sugar from 100 parts of wood.

In some paper manufactories the saccharification is carried out in the following manner. About a couple of tons of deal shavings are placed in a large vessel containing about 1,760 gallons of water and 16 cwt. of crude hydrochloric acid, and the whole is kept at the boiling temperature for 13 hours by means of a current of steam. The acid liquor is then drawn off, and 99 per cent. of the free acid is neutralised with carbonate of lime, free carbonic acid being formed, and calcium chloride, which does not interfere with the operation of fermenting. Fermentation is set up by the addition of yeast, the temperature of the liquor being kept at 22° to 25°C. In the subsequent distillation a quantity of alcohol is obtained corresponding to the sugar previously formed.

The residual wood stuff is submitted to a methodical washing, then crushed under a mill-stone, again washed, freed from mechanical impurities, drained and pressed. In this way a brown wood stuff is obtained, that is very suitable for the manufacture of packing paper.

A better and lighter paper is obtained when the wood paste is submitted to strong pressure in a hydraulic press, so as to form cakes about $\frac{1}{8}$ in. thick, which still contain 60 per cent. of water. These are formed into cylindrical rolls, and in this condition are bleached for 36 to 48 hours in a chlorine chamber. A reddish wood stuff is thus obtained which can be used directly for the manufacture of ordinary paper.

For the production of a white stuff, the wood mass, after its removal from the chlorine chamber, has to be thrice macerated in lime water, each 100 parts of which has been treated with 10 parts of soda at 80° to 90°C. Lastly, the paste is thoroughly washed in a vessel provided with a sieve bottom. At the same time the mass is perfectly bleached by chloride of lime mechanically distributed through it, which leads to a loss of 30 per cent.

The considerable loss of cellular substance during the preparation of wood for the paper manufacture is dependent on the use of chlorine gas or chloride of lime, it being difficult to limit the action of these substances to the colouring and incrusting matters of the wood. If the quantity of these agents be rather too large, or the temperature be too high, a portion of the cellulose is burnt to carbonic acid and water. In some measure this may be prevented by using less chlorine or chloride of lime, and allowing them to act at a lower temperature but for a longer time.

The cost of paper stuff, prepared according to the chemical method from wood, is much less than that of rag stuff, to which it can be added to the extent of 80 per cent., but only 20 per cent. of the mechanically prepared wood stuff can be so added. The price of the latter however is so much the lower, that at present it is more extensively used than the chemically prepared.

G. Fry treats the wood in fine shavings with water and high pressure steam only, and works the liquor running off and pressed from the shavings for alcohol.

Straw, by proper treatment, yields a paper stuff which is preferred to that prepared from wood, and in many manufactories in Germany and other countries a very large quantity is now made from straw. The fibres obtained from straw by suitable treatment are thin and smooth, easily felted, and yield a close, firm paper, but which, when it consists only of straw, is brittle. The straw stuff is therefore also used together with rag stuff, to which it can be added to the extent of 80 per cent. without the paper becoming too brittle for ordinary use. For instance, the paper on which some newspapers are printed consists of two parts of straw and only one of rags.

The preparation of the straw is partly mechanical and partly chemical, and on the whole is rather troublesome. In a large manufactory at Krollwitz, near Halle, it is carried on according to the following method originally introduced by Keferstein, but known as Lahousse's method.

The chopped straw is placed in a large vertical sheet-iron cylinder, which revolves round a hollow axis; the apparatus is then completely filled with a solution of caustic soda, prepared with lime from the very best soda. The manhole is closed, and during four or five hours the cylinder containing the cold ley is rotated. After this the caustic soda is drawn off from the chopped straw and pumped into the ley reservoir ready for a new operation.

During this treatment with cold caustic soda, the greater part of the incrusting material of the straw, principally gum and protein stuff, is washed off; the silica, of which the straw contains as much as 5 per cent., is not attacked.

After the soda ley has been drained off from the straw as much as possible, the drum is turned so that the straw falls out through the open manhole into the steamer, which usually is arranged similarly to the revolving rag boiler. When the steamer is filled with straw superheated steam at 150° is admitted through the hollow axis. As soon as the entire mass has acquired the temperature of the steam, hot water is run in, which causes the steamer to rotate. After a time the wash water is run off and steam at 150° is again admitted, and this treatment is repeated six or seven times. At the commencement of the process, the pores of the straw are still full of absorbed ley. When the steam is admitted this forms a hot ley, by which the silica, unattacked by the cold ley, is converted into soluble sodium silicate. By the succeeding treatment with warm water this is dissolved and washed out. As the disengagement of the silica, however, is only effected slowly, the operation, as before stated, has to be several times repeated.

It is very essential that the silica should be removed as completely as possible, because otherwise the paper manufactured from straw stuff is transparent.

The bleaching and crushing of the straw mass, which operations follow next, are carried out simultaneously. The steamed and washed straw is removed from the steamer and put with chloride of lime into a large bleaching and pulping vessel, about 10 or 15 pounds of the chloride being added for each hundredweight of straw originally used. After the entire mass has been reduced to a pulp, it is brought into tubs standing on a lower stage, in which the straw is prevented from settling by the motion of a stirrer. It is then raised by a pump and run through a trough between two ordinary millstones, by which means all the knots, ears, etc., are crushed, and made accessible to the action of the chlorine. Decomposition of the chloride of lime by the addition of an acid is not necessary, as decomposition is sufficiently effected by the heat of the friction generated in passing between the millstones.

If it is intended to send the material into the market, the bleached mass is pressed. If, on the other hand, it is to be worked up at once into paper of the ordinary sort, it is run directly into the tubs over the paper machine. But if it is to be used for finer paper, it is previously allowed to stand upon porous stone, by which the greater part of the lime liquor is absorbed.

According to Keferstein, the yield of fibre by this method amounts to 55 per cent. of the straw used. If the straw be at first treated with hot instead of cold soda ley, the yield diminishes to 40 per cent. Wood in the rasped condition can also be prepared for paper stuff by this method.

Straw can also be treated according to the method before described, as followed at the Pontcharra works, in the preparation of wood stuff (p. 635). The straw is chopped into pieces ½ in. to 1 in. long, and then treated in the same way as the wood with hot or cold aqua regia, washed, crushed, again washed and bleached. By Berges and Zuber, and Rieder, the straw is cut in a machine, freed from knots in a kind of powder mill, crushed and ground by a cylinder, and washed for ten or twelve hours in a rotatory apparatus; 25 to 30 parts of 90° soda dissolved in 200 parts of water being used for each 100 parts of chopped straw. The wash liquor is drawn off, and united with that obtained by strong pressure of the straw between cylinders, concentrated by hot air drawn from the flue of a reverberatory furnace, and finally brought to dryness and calcined in the furnace itself. A salt mass is thus obtained which, after lixiviation and treatment with lime, yields a caustic ley that can be again used for the washing of straw. The washed straw mass is pressed, dipped in warm water, then washed in cold water, the fibres being at the same time again separated. The bleaching is done in the same vessel as the washing, by means of chloride of lime.

Preliminary Treatment of the Rags.—When rags are used for the manufacture of paper, the operations commence with the sorting of the rags, which is not done with sufficient care by the rag collectors. The work is usually done in the basement of the factory by women and girls, and with it was formerly combined the cutting up of the rags. The workers stand before a kind of table with a wire net surface, upon which the rags to be sorted are spread out, and the rags are cut by a perpendicularly fixed knife; the new rags into pieces 2 in. wide by 5 in. long, and the old rags into pieces 4 in. wide by 6 in. long. At the same time all the hooks, buttons, seams, and especially all hard parts of the rags are removed; the rags being thrown according to their quality into various receptacles. During this operation a large quantity of dirt from the rags falls through the wire surface into a receptacle underneath. At the present time the cutting up of the rags is sometimes done by a special machine.

The degree to which the sorting is carried out differs in various manufactories. In some the rags are sorted only according to the material from which they are woven, into linen, cotton, silk, and woollen; more generally the sorting is carried further, and extends to the colour and the form in which the fibre occurs in the rag. This more

thorough sorting, however, applies only to the linen and cotton rags, because only those are used for the better sorts of paper.

The principal object of the sorting is to bring together as nearly as possible rags of the same quality, so that in the succeeding operations of washing, bleaching, and pulping, a material as nearly equal as possible in colour and texture may be used. If dirty rags be washed with clean, or coloured rags bleached with white, the latter are under treatment much longer than is necessary. The same holds good for the pulping in the hollander, which is worked much more rapidly for open texture than for close.

The apparatus used for cutting the rags is of various construction. The simplest and oldest is in principle the same as a straw cutter. The rags are pushed under a fixed horizontal band, in front of which, and just in contact with the edge, a sharp knife passes up and down in a vertical direction. Sometimes instead of a vertical the knives have a rotary motion.

Fox's rag-cutter consists of two horizontal cylinders, surrounded by sharp steel edges at intervals corresponding with the size to which the rags are to be cut. The cylinders are placed so that, when they revolve, the knife edges of one fit exactly over those of the other, and the rags are passed between them, the machine being fed through a funnel.

The purification of the rags is divided into a dry and a wet cleansing. The first is partially effected in the sorting and cutting, during which a considerable quantity of dirt falls through the wire gauze. After leaving the cutting machine, the rags are passed into a sifter, consisting of a large cylinder covered with wire gauze, and revolving round a wooden shaft. Upon the cylinder being set in motion the rags are tossed about, and the dirt falls through the wire gauze into a surrounding wooden frame, from which the dust is carried forward by a current of air. The length of the cylinder is from 7 to 10 feet and the diameter about 32 inches. Instead of the revolving cylinder, a stationary one is sometimes used. In this the rags are beaten by wooden arms set spirally round a revolving shaft and reaching almost to the periphery of the cylinder; the shaft makes 150 to 200 revolutions per minute.

The loss during this operation (independent of loss of weight representing moisture) amounts with fine clean rags to from 1–1·5 per cent.; for hems and seams, to 2·5—3·6 per cent.; for coarse rags, packing cloth, rope, and string, which have to be very thoroughly shaken, to 4–5·5 per cent.

In order to avoid the inconvenience of stopping the machinery for the emptying and filling the cylinder, a continuous apparatus has been introduced. It consists of a stationary conical sieve cylinder, having a shaft passing through it to which are fastened wooden or iron beating arms. The rags are introduced at the narrow end of the cylinder, fall towards the opposite side, and are thrown out purified at the wide end.

In most manufactories the rags are not washed in water alone, but are carried directly from the sifter to the boiler. When they are so washed, the washing is done in a horizontal wire gauze cylinder, revolving on its axis in a trough of water, like a beet-washing cylinder (see SUGAR).

In order to remove greasy dirt, and to destroy many colours preparatory to the bleaching process, the purified rags are boiled in a caustic ley. For the finer rags, soda potash or caustic soda are used; for the coarser, caustic lime, sometimes with the addition of some soda. In the older paper manufactories, 10 to 20 parts of caustic soda are taken for each 1,000 parts of rags, according to their quality. When the rags have not been previously washed with water, they are first moistened with warm water, then thrown on the heap, and afterwards brought into the boiler, which may consist of an open or closed stationary or revolving vessel.

Payen gives the following proportions of lime and soda for 100 parts of different kinds of rags:—

	Lime.	Soda.
Hard and dirty rags	15	6
Strongly coloured rags	12	3
White rags	5–10	0

E. Hoyer gives the following proportions:—

	Lime.	Soda.
Fine white well-worn rags	0	5
Fine, less worn	15	1
Half fine, not quite white	20	1
Coarse unbleached	25	0
Fine coloured	15	15
Coarse coloured	20	0

According to Hoyer, the finer rags are best treated with soda only, whilst for the coarser he recommends an addition of caustic lime, or the lime alone. The lime is

converted into a fine milk and mixed with the dissolved soda before adding to the rags.

The stationary boiler is a large vessel heated by steam. It is provided with a perforated false bottom, situated a short distance above the real bottom, and upon which the rags are placed. The boiler being then partly filled with the ley, the steam is admitted into the interspace between the two bottoms, passing either directly into the ley or first through a spiral. The ley is thus heated, and is driven upwards through a vertical copper pipe, which opens towards the top of the boiler; from thence the ley falls on to the rags, and permeating through them, drains through the perforated bottom into the interspace, where it is again heated and driven upwards through the copper pipe. The operation lasts from four to six hours, after which the liquor is run off through a tap placed below the perforated bottom, and the rags are again boiled with water.

The boiling is carried out much more effectively and quickly in a vessel having a rotatory movement, the rags being thus brought more perfectly into contact with the ley. The apparatus of Bryan Donkin consists of a spherical boiler, about 8 feet in diameter, supported at the two ends of its hollow axis upon a strong cast-iron frame. The boiler makes two revolutions in four or five minutes. Through one end of the hollow axis water can be run into the boiler from a reservoir placed at a higher level, or by means of a pipe fixed in it the liquor can be pumped out of the boiler. Through the other end steam may be admitted from a steam chest situated below the boiler and ley from a reservoir above. The steam passes from the hollow axis through a pipe into a kind of cylinder sieve, fixed in the middle of the boiler, and constructed of twelve perforated sheet-iron plates, the holes being $\frac{1}{8}$ in. in diameter, and $1\frac{1}{4}$ in. apart. This cylinder, which is about 4 feet wide, guards the end of the steam pipe from becoming stopped up by the fragments of rag, and also distributes the steam over a large surface. Over the surface of the cylinder, at intervals of about 2 feet, are teeth, by which the rags are beaten up during the rotation of the vessel. The filling and emptying of the boiler with rags are effected through a round manhole, and the dirty liquor is drawn off through a tap. The spherical vessel will hold a ton of rags at one time, and only requires one-sixth of a horse-power to set it in motion. Its efficiency may be increased by fixing pegs on the inner surface, which set up a brisker agitation of the rags; also by increasing the pressure of steam to 3 to 5 atmospheres, thus raising the temperature of the contents to 133° to 152°. The height of the liquor is observed through a small tap fixed in the side of the vessel; at the commencement of the operation it should not exceed one half the height of the boiler, and at the finish not exceed two-thirds.

In filling the apparatus the manhole is brought directly under a shoot through which the rags fall; the rags are pressed together with a lever or by treading them down, and when a sufficient quantity is admitted, the manhole is closed. The milk of lime or other caustic liquor is then run in through a tap until its level reaches half-way up the vessel, and afterwards the steam is admitted through one tap, another being opened to allow the excess to escape. After three or four hours' boiling, both taps are shut off, but the rotation is continued three hours longer, and then the caustic liquor and condensed steam are run off, and a stream of fresh water is allowed to pass through the rags for two hours. The average time required for the entire washing is twelve hours. The height of the liquor is never allowed to be increased by the condensed steam beyond two-thirds, the excess being run off through a tap. When the boiling is finished, the lid is taken off the manhole and a half turn given so as to bring the opening underneath; water is let in and the rags are washed out and fall into a receiver beneath, which is provided with a sieve bottom, through which the water can drain away.

An apparatus for boiling with ammonia has been before described (p. 636) in the preparation of wood paper stuff, and can be used with advantage in the boiling of rags.

Pulping of the Washed and Boiled Rags.—Before bleaching, in order to present the largest possible surface to the action of the bleaching agent, the rags require to be disintegrated. This, however, must not be carried too far at once, as the washing of a finely-divided mass would be very difficult. The preparation of the paper pulp is therefore divided into two stages: (1) partial disintegration before bleaching; (2) complete disintegration after bleaching. The product is called **half stuff** or **whole stuff**, according as it has gone through both, or only one stage.

Formerly the disintegration of the rags was effected, according to the German method, by stampers; but at the present time only the Dutch method is followed. The apparatus in which the rags are reduced to a pulp by the Dutch method is called a **hollander**, and, according as it is used in the preparation of half stuff or whole stuff it is called a **half hollander** or a **whole hollander**.

At the same time as the rags are reduced to pulp in the hollander they are also thoroughly washed.

The hollander (figs. 439 and 440) consists of a large shallow trough, about 10 ft. long, 5 ft. wide, and 20 to 25 inches deep. It is divided into two equal portions by an upright partition (A A) running lengthways, the ends of which do not reach the ends of the trough, a free space being left equal at each end through which the rags and the liquid can circulate round the partition. The trough is generally made of wood, lined with sheet copper or lead. Recently, however, cast-iron hollanders have been coming more into use; these do good service, but they cannot be used for the bleaching of the paper stuff with chloride of lime and acids, unless they are first coated with cement, because the iron would be attacked. Stone troughs, and troughs made of pieces of stone and cement, are also used, and, especially the latter, are much approved.

On one side of the apparatus are the pulping cylinders (C C), the axes of which are supported at one end by the side of the trough and at the other by the partition in

FIG. 439.

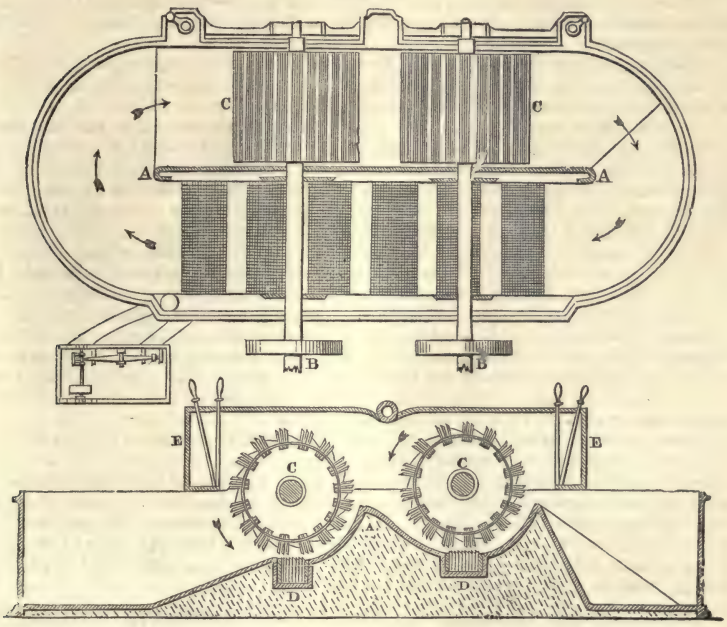


FIG. 440.

the middle called the midfeather (A A); they then extend through the other side of the machine, where they are driven by pulleys fitted on to the projecting ends of the shafts (B B). The cylinders are fitted in the direction of the axis with cutters, which are generally made of steel, but where bleaching with chlorine is carried on in the hollander they are made of bronze (85 per cent. of copper and 15 per cent. of zinc). The number of knives in the cylinder of a half hollander varies from 30 to 50; in a whole hollander it varies from 65 to 75. Below the cylinders are frames (D D), generally of cast iron, set with sharp knives at a slight angle with those of the cylinder, so that, upon the cylinder being rotated, a cutting action is set up between the two sets. The knives are fastened in their respective places by wooden plugs.

The rags being in comparatively large pieces when first put into the hollander, the space between the knives in the cylinder and those beneath has at first to be wider than it is afterwards, and for this purpose there is an arrangement by which the axis of the cylinder can be raised or lowered as required.

The rags being put into the hollander, together with a quantity of water, and the cylinder set in motion, a circulation is established, the rags being carried by the current of water between the cylinder and the fixed cutters and thus disintegrated.

The cylinder makes 180 to 220, or even 240 revolutions in a minute; it is worked less rapidly in the half hollander than in the whole hollander.

At the same time as the disintegration of the rags takes place a further cleansing is effected, dirt being removed from between the tissues which the previous washing and boiling could not touch. For this purpose a constant flow of water is kept up. The soiled water escapes through wire-gauze screens, fixed behind and before the cylinder. By the action of the cylinder, the rags and water are flung against these screens; the water passes through and runs away through the outflow pipe, and the rags remain partly adherent to the screen and part fall back into the trough. When the mass has been sufficiently washed, the wire screens are covered over, and the supply of fresh water is stopped; the pulping process is then continued alone.

A more convenient contrivance is the washing cylinder, the circumference of which is formed of wire gauze. The water passing through this into the cylinder is carried by spirally arranged pipes into the hollow axis from which it passes into an outflow pipe. The washing cylinder makes about twenty revolutions per minute; it is at first set in motion by special machinery, but afterwards the motion is kept up by the current of the liquid in the hollander.

In order to separate any sand present, there is a trough running across the bottom of the hollander, covered with wire gauze, through which the sand falls into the depression beneath.

Each hollander is charged with 1 to 2 cwt. of rags, the water required being from 250 to 450 gallons. The entire operation lasts from two to four hours. The emptying is effected through an opening at the bottom of the hollander.

In most paper manufactories this first pulping work is carried out in a half hollander, and for white rags, which are easily washed and pulped, it is sufficient. But for coarse, hard rags, as well as seams, cord, etc., which are very difficult to pulp, Planche recommends the use of two hollanders, which should be so fixed that the pulp can flow from one into the other. In the first the operation is chiefly directed to washing the rags; in the second the pulping is carried on. The cylinder of the first hollander is set with 36 knives and there are 6 or 8 fixed knives; these are sufficient for the beginning of the pulping process; it makes 150 revolutions per minute. There are besides in this hollander a washing cylinder, washing screens, and two sand-catching troughs. The cylinder of the second hollander is set with 54 knives and there are 10 or 12 fixed knives; these knives are also thinner. The revolutions amount to 180 in the minute. The wire gauze of the washing cylinder is finer than in the first hollander; the washing screens are not used. The operation lasts four hours. The loss varies, for good rags, between 7 and 14 per cent., and for inferior rags, seams, rope, etc., between 18 and 35 per cent.

The paper stuff from the second hollander is allowed to run into a vat, the bottom of which is made of wire gauze. After it has drained, it is conveyed, in many factories, upon an endless cloth between a pair of gutta-percha or hardened caoutchouc cylinders, and the adhering water expressed as much as possible. A cake of paper stuff is thus obtained about a quarter of an inch thick, containing 60 per cent. of water and 40 per cent. of dry stuff. Recently Rieder has recommended the removal of water from half stuff by submitting it to the action of a centrifugal apparatus making 1,200 to 1,300 revolutions per minute.

Bleaching.—The bleaching of paper stuff has for its object the destruction of colouring matter, and the conversion of the stuff into as white a mass as possible. The operation is carried out with chlorine gas or chloride of lime.

In bleaching with chlorine gas, the chlorine prepared from manganese and hydrochloric acid, according to one of the methods described on p. 163, passes through leaden pipes into the upper part of the bleaching chamber. The half stuff having been sufficiently freed from water, and, if it has been pressed, again separated by the action of the wolf, a shaft armed with teeth and revolving in a trough is spread out upon wooden shelves in the chamber. The chlorine entering at the top, makes its way by virtue of its greater specific gravity towards the bottom, passing through the stuff on the upper stages to that on the lower, the excess of chlorine escaping through an opening at the bottom into an adjoining bleaching chamber.

The chambers may be replaced by several bleaching chests, about 3 feet high, and filled with paper stuff. The chlorine is introduced into these chests also at the top, and the bleaching is completed in ten or twelve hours.

Instead of tearing up the stuff which has been pressed between rollers, the cakes may be rolled up loosely and the rolls stood side by side in a receptacle about 16 feet long, 5 feet wide, and 4 feet 2 in. deep, constructed of brickwork, the inside of which is coated with tar and lined with wooden planks, whilst the outside is coated with either wood or stone, all crevices being well stopped up. The washed and

cooled chlorine is admitted at one end into the upper part and makes its way towards the opposite end, displacing the air. Each receptacle of the dimensions given will contain two tons of dry paper stuff. In working a system of 13 receptacles, 3 are being charged, 3 are being emptied, 6 are in action, and one is under repair.

If the temperature be too high during the bleaching process, the action of the chlorine upon the paper stuff is too energetic; it attacks the cellulose and in this way a loss of much fibre substance may result. The temperature must therefore be kept as moderate as possible, and the chlorine should only be admitted in small quantities at a time. But at too low a temperature the bleaching goes on slowly, and then the temperature has to be raised by the admission of a little steam.

After the paper stuff has been bleached with chlorine gas, it is placed for further draining in boxes, where it lies for 24 to 48 hours, during which time it undergoes an after bleaching from the still adhering chlorine.

In order to wash and pulp the bleached mass at the same time it is put into a hollander, the knives in which are of bronze, as steel knives would be too strongly attacked by the chlorine.

Bleaching with chloride of lime.—Latterly chloride of lime has been used for bleaching in by far the most paper manufactories. The chloride of lime, or bleaching lime, contains the active constituent calcium hypochlorite, which upon the addition of hydrochloric acid is decomposed into calcium chloride, water, and chlorine. Instead of hydrochloric acid, sulphuric acid may be used, because this decomposes any calcium chloride present in the chloride of lime, with formation of calcium sulphate and hydrochloric acid, the hydrochloric acid then reacting upon the calcium hypochlorite and liberating chlorine.

For the purpose of bleaching with chloride of lime, a clear solution of it is prepared and added, together with hydrochloric or sulphuric acid, to the paper stuff. The mixing is effected in a hollander which has usually double the capacity of those previously used. This hollander is constructed of wood, cement, etc., or even occasionally of cast iron; in the latter case, the interior must be coated with cement or the iron would colour the paper mass. Instead of steel knives, the cylinder and the frame below are best provided with wooden cutters. Washing screens are not used, but sometimes a sand-catcher, and here and there a couple of washing wheels. In the place of the cylinder furnished with wooden bands, there is in many hollanders only an axis upon which between two wooden disks are six or eight wooden shovels; these should be covered with sheet lead to protect the wood from splintering. The rotation of these shovel wheels must be sufficiently rapid to communicate to the liquid the same rate of motion as in the ordinary hollander.

In order to accelerate the washing and bleaching, Planche uses instead of the shovel wheel one set with bronze bands, and beneath it a frame furnished with three similar bands. He also recommends a simple arrangement for supplying the bleaching liquid or water. It consists in providing the hollander with a perforated double bottom made of bronze plates and having the holes one-twelfth of an inch in diameter. At the side is a smaller tank of wood communicating through the bottom with the space below the false bottom of the hollander. At a higher elevation are fixed three vessels,—one containing fresh chloride of lime solution, one a weaker liquor that has been already used once, and the other water,—and from each of these a pipe having a tap at the end passes into the small wooden tank. Upon a tap being opened, the liquor runs from the respective vessel first into the small tank, and then from it through the false bottom into the hollander.

Frequently, especially in large factories, bleaching with chlorine gas and with chloride of lime are combined, the rags or half stuff undergoing a first bleaching with chlorine gas in bleaching closets or boxes, and an after bleaching with chloride of lime solution in the hollander. More often, however, both bleachings are effected with chloride of lime, but in this case the after bleaching is carried out on the whole stuff.

The quantity of bleaching material required varies according to the nature of the paper stuff to be bleached, as well as with the strength of the bleaching material. In bleaching with chlorine gas there is required, on the average, for 100 parts by weight of dry stuff, 4 parts of manganese and a corresponding quantity of crude hydrochloric acid. When chloride of lime is used, the quantity required for 100 parts of stuff varies, according to its strength, between 1 and 8 parts and ½ part of sulphuric acid. The sulphuric acid is diluted with twenty times as much water, and added to the chloride of lime solution, a small quantity at a time.

It is very important that before further working the bleached half stuff it should be perfectly washed. With this object there is in the bleaching hollander a washing cylinder, by means of which, after the bleaching is completed, the half stuff is thoroughly washed. When the greater part of the chlorine has been removed by the

water, a small quantity of sodium hyposulphite (antichlor) dissolved in water is added; this is oxidised to sodium sulphate by the bleaching material still adhering to the stuff, and the whole can then be easily removed with water.

The bleached and washed half stuff is now brought to as fine a pulp as possible in the whole hollander, and is then called whole stuff. The difference between the whole hollander and half hollander, as before explained, consists chiefly in the pulping cylinder and frame of the former being provided with more and finer knives, so as to effect a more complete disintegration, and the absence of the washing screens. The pulping of the paper is carried on in the whole hollander in the same manner as in the half hollander, but it requires more care, as the disintegration may easily go too far, a result that is called dead pulping. The time required for this stage is about the same as that taken up in the preparation of the half stuff.

Planche distributes the work of the whole hollander between two hollanders, one of which stands at a higher elevation than the other, so as to allow its contents to pass from the upper one into the lower. In the first the half stuff coming from the bleaching hollander is thoroughly washed with water. As soon as this is accomplished the supply of water is stopped, but a part of the water is still allowed to run off through the washing cylinder, so that a denser mass remains. Meanwhile the pulping cylinder is lowered into the hollander, and a pulping process is commenced, which, after the stuff has upon the opening of a valve passed through into the second hollander, is there completed. By this arrangement the pulping of the whole stuff is effected in two or three hours.

The mixing of the various kinds of stuff to form a paper stuff of certain quality is carried out in the whole hollander, and the greatest care has to be used in the selection and proportions of the sorts mixed. For instance, a stuff from coarse rags must not be mixed with one from fine rags, as the resulting paper would be rough and unequal, and the finer stuff would be so far wasted. In order to obtain a fine paper, only stuffs as nearly as possible of similar character should be mixed together, the fine-fibred with the fine-fibred, and the coarse-fibred with the coarse.

Lately, a considerable proportion of wood stuff or straw stuff has been added to that from rags in the preparation of the better kinds of paper. Thus, in the factory at Krollwitz near Halle, 66·6 parts of rag stuff and 33·3 parts of straw stuff are used in the making of fine letter paper, and 33·3 parts of rag stuff and 66·6 parts of straw stuff in the making of good writing or printing paper. Wood stuff cannot be added in so large a proportion. According to C. Hoyer, 15 to 30 per cent. may be used for a medium-fine writing and printing paper; 30 to 50 per cent. for ordinary writing and printing paper; 50 to 80 per cent. for ordinary paper-hangings, bottle and packing paper; millboard and pasteboard may be made entirely from wood stuff.

Tinting.—In order to give to the paper a greater whiteness, as well as to increase its weight, the so-called dressing is sometimes added to the whole stuff. This coats the separate fibres and fills up the interspaces of the felted mass. Only a finely-powdered beautifully white material can be used for this purpose, such as baryta white, heavy spar powder, gypsum, washed chalk, or perfectly white kaolin powder; lead sulphate and lead white are also used. The 'pearl-hardening' that is imported from America is an artificially prepared silicate of lime. The chalk and fine white clay in the form of kaolin, or some other preparation of clay, are to be preferred, because the paper has a more uniform appearance than when the specifically heavier and consequently more difficultly distributed baryta or lead compounds are used. The quantity of dressing added amounts to from 10 to 20 per cent. of the weight of dry stuff. Too much should not, however, be used, or the weight of the paper would be increased at the cost of its quality.

As it is generally desired that a paper should have a somewhat bluish tint, whilst the bleached stuff always still retains a trace of yellow, it is usual to add some blue colouring material to stuffs intended for fine papers whilst still in the hollander. Ultramarine is most frequently used for this purpose, about 1 per cent. of the weight of stuff being added, more or less according to the shade required. Instead of ultramarine, smalt, indigo, or prussian blue may be used: but the first has the advantage that it can always be obtained in commerce, already reduced to a sufficiently fine powder.

Sizing.—In consequence of the felt-like texture of unsized paper, it absorbs like a sponge any liquid with which it comes into contact; it is therefore quite unsuited for writing upon. In the preparation of writing papers the interstices between the fibres have to be stopped up by some glutinous material such as size.

The operation of sizing can be carried out in different ways. Formerly only the finished sheet of paper was sized, but now the size is generally added to the paper stuff whilst in the tubs or in the hollander. The first method is called sheet-sizing, the second tub-sizing.

The sheet-sizing is usually done with ordinary animal size only, but it is neces-

sary that this should be as colourless as possible in order not to injure the colour of the paper. The size used for the purpose is prepared from the skins of hares and rabbits, the hoofs of sheep and goats, parchment refuse, eel skins, etc. These materials are washed, then steeped in lime water, and afterwards perfectly cleansed from it by washing in acidulated and then in pure water. It is next gently boiled in 8 or 10 times its weight of water for six hours, during which time it is sprinkled with a small quantity of very finely powdered lime, in order to convert the fat into an insoluble lime soap. As soon as a drop of the liquor placed upon a cold porcelain plate solidifies to a jelly, the boiling is completed. To 100 parts of this jelly is added 2 or 3 parts of alum previously dissolved in water, by which the size is coagulated and rendered insoluble, and consequently is in a more suitable form for the sizing of paper. The same quantity of jelly is required, whether added to the stuff in the vat or to an equal quantity of paper. Practically the ready-made size of commerce is used. This is steeped for two or three hours in water and then dissolved in boiling water; 13 to 18 lbs. of size mixed with 4 to 6 lbs. of alum, dissolved in 22 gallons of water, is sufficient for the sizing of a whole vatful of paper.

The solution of size is brought to a temperature of 25°, and then about 100 sheets of paper are dipped into it at one time, and so moved about that each sheet becomes coated with size on both sides; they are next pressed so as to distribute the size in the interior of the separate sheets, and afterwards separated and hung to dry on lines in a drying room. The greatest caution has to be exercised in the drying; it must in general go on slowly, without however lasting sufficiently long to allow of decomposition of the moist size to take place. This decomposition is induced sometimes during thunderstorms in summer; the size is covered with mould, becomes liquefied, and loses its glutinous properties. If the paper be too rapidly dried the size remains distributed throughout the whole mass; whilst during a slow drying the size is drawn, together with the moisture, to the surface, and there forms an impermeable layer. For this reason a paper sized in sheets will blot if written upon where the sized surface has been scraped off.

In tub-sizing the size is added to the stuff in the tubs or in the hollander; the paper prepared from it is therefore uniformly sized throughout the whole thickness. Ordinary animal size is seldom used for this operation; but much more generally a resin soap and alum, or aluminum sulphate, or resin soap, aluminum sulphate and starch together, are used. The respective quantities of these substances used are generally a secret in each manufactory. In the following description the quantities recommended by Planche are stated.

In order not to injure the whiteness of the paper, upon which much of its value depends, it is necessary that the purest and whitest resin and starch be used. Of the different kinds of resin the French and American have the preference. They are the residues obtained in distilling turpentine with steam in the preparation of oil of turpentine, and are usually known as colophony. This resin is either only slightly yellowish or quite colourless.

For the paper manufacture a specially white and pure starch is made. It contains at the most not more than 18 per cent. of water, which is tested by the loss of weight of a weighed quantity at 110°. The ash should not amount to more than 3 to 4 parts per 1,000; a larger quantity would indicate a fraudulent admixture.

The alum, or aluminum sulphate, used for breaking up the resin soap must be perfectly free from iron; this may be tested by dissolving it in water, and adding potassium ferrocyanide, which should not produce a blue precipitate even upon the addition of some drops of chlorine water. Alum has the advantage over aluminum sulphate that in consequence of its power of crystallisation it can more easily be obtained pure. On the other hand, the aluminum sulphate is lower priced, and if it can be obtained free from iron it is more profitable.

In the preparation of the resin soap 22 lbs. of caustic soda are dissolved in a boiler in about 160 gallons of water, and brought to the boiling point by the introduction of steam. To this 220 lbs. of powdered and sifted resin are added gradually, and the boiling of the liquid is continued until the resin is completely dissolved; it is then allowed to stand quietly for two days in a settling vessel to deposit suspended matter. On the other hand, 1,100 lbs. of aluminum sulphate are dissolved by heating with steam in 110 gallons of water. This quantity is sufficient for the sizing of the paper stuff from 166 hollanders, reckoning 10 pints of solution for each, corresponding to about 6½ lbs. of aluminum sulphate. In a special vessel 22 lbs. of starch are stirred up in 11 gallons of water, and this is poured into about 160 gallons of the resin soap liquor, where it is heated by steam to 100°, and then added to the paper stuff in the hollander whilst in operation. After the soap has become thoroughly distributed amongst the pulp 10 pints of the aluminum sulphate solution are added, which fixes the size in the fibre of the paper.

The results obtained by the above operation are briefly as follows. By the introduction of the resin into the boiling soda ley, soluble compounds of the soda with the acids of which the resin consists (abietic acid, etc.) are formed. The soda-resin soap is therefore a compound of sodium resinate soluble in water. When this solution is mixed with a solution of aluminum sulphate a double decomposition takes place, sodium sulphate and aluminum resinate being formed. The former dissolves in the water; the latter is the size, which, being insoluble in water, separates out as a jelly-like substance. When the mixing of the solutions is effected in the hollander the size is precipitated as an extremely fine coating of the paper fibres.

Frequently, however, the mixed size is adopted. In this case a mixture of resin soap containing about 4½ lbs. of resin, 8¾ lbs. of starch, and 4½ lbs. of size previously dissolved in water is put into the hollander, and solution of aluminum sulphate is added until the liquid gives quite a weakly acid reaction.

In general it may be stated that in the sizing for writing paper of 100 lbs. of paper stuff (dry) there is used 1 to 1¼ lbs. of soda, 10 to 12 lbs. of resin, 20 to 30 of starch and 5 to 6 lbs. of aluminum sulphate.

In the sizing of ordinary paper, a cheaper tallow or oil soap is used in place of the fine resin soap. According to Hoyer 100 lbs. of stuff take 3 lbs. of soap and 3 lbs. of alum. For very fine paper on the other hand a wax soap is used, made by dissolving 40 lbs. of wax in a potash ley, containing 10 lbs. of potash and 5 lbs. of caustic lime. This soap is added to the stuff in the proportion of 2 lbs. of wax to 100 lbs. of stuff, and to this is added 3 lbs. of alum or 1¼ lbs. of aluminum sulphate.

Paper Making.—According to the older methods, the conversion of paper stuff into paper was effected by hand labour, paper machines being of comparatively recent introduction. L. Robert, of Esonne, France, was the first to construct, in 1798, a small machine, and bring it into use. In Germany the first paper machine was set up at Weida, in 1819, by A. Keferstein.

Hand Paper.—The manufacture of hand paper is at the present time only of secondary importance; it requires too much time and skilled labour for it to compete with machine-made paper. Only paper for special purposes, such as filtering paper, is now made by hand.

The contents of several hollanders are united in one large vat, and diluted with water to form a thin milky paste. Across the top of the vat is a perforated plank called the great bridge. During the operation the pulp in the vat is kept continually stirred to prevent the fibre from settling to the bottom, and it is also kept warm either by the admission of steam or by a special furnace. The formation of the paper is accomplished in the so-called mould which is a rectangular wooden frame, spanned with fine wire gauze, and corresponding to the size of the sheet of paper required. This mould is dipped by a workman into the paper pulp and lifted out again in a horizontal position, so that it remains filled with pulp to the height of the movable sides or deckel of the frame of the mould. The water drops through the meshes of the gauze, leaving the fibre upon the wires to form the sheet of paper, a process which is hastened by shaking the frame. The water falls back into the vat, but in order to prevent the pulp from becoming thus too much diluted, fresh stuff is added from time to time. The thickness of the paper therefore is dependent upon the consistency of the pulp and the height of the side or deckel of the mould.

After the greater part of the water has run through, the mould is placed for further draining on the bridge. A second workman then reverses the mould, so as to bring the paper underneath, upon a sheet of felt, an operation that is termed couching. Upon the removal of the mould the paper is left upon the felt. On this is placed another sheet of felt, then another of paper, and this is repeated until a post is formed, consisting of sheets of paper and felt alternately. The post is allowed to stand some time that the felt may absorb the water, and then it is placed in the press and pressure applied so long as any water runs away. The sheets of paper and felt are then separated, and paper of good quality is submitted to the same operation once or twice more, but ordinary paper is at once dried after the first pressing. In order to prevent mould, the felts require to be occasionally dried. The paper is dried by hanging it on lines in a suitable drying room.

Machine Paper.—In the manufacture of machine paper, the paper stuff from at least six hollanders is brought into a large common reservoir, where it is diluted with water according to the thickness of the paper to be made; for thick paper only a small quantity of water being added, and for thin paper more. A stirrer is kept continually in action to prevent the fibre sinking to the bottom. From the reservoir

the pulp passes into the vat, a special mechanical arrangement being used to regulate the flow. From the vat it passes to the paper machine, but before doing so it is frequently subjected to an operation for the removal of any sand or lumps present. The objects sought to be attained in the paper machine are to remove the greater part of the water from the pulp, to effect the felting of the fibres, to form the sheet of paper, and finally to dry the latter. The pulp flows first on to an endless band of wire gauze, which is carried forward on a number of small rollers, by which arrangement the web is kept in an exactly horizontal position. On each side of the wire gauze, and travelling at the same rate, is an india-rubber band, forming the sides or deckel. The draining off of the water and the felting of the fibres is hastened by a jogging sideways motion. As the pulp is carried forward on the gauze band, the principal part of the water falls through the meshes, whilst the fibres remain and become more and more compacted into a sheet of paper. The water collects below, and is raised by a turbine arrangement again to the reservoir, where it is used for the thinning of a fresh quantity of stuff from the hollanders. A further portion of the water is removed by passing the gauze band over a series of open chambers where the pulp is subjected to the action of an aspirator. Kaufmann's apparatus, which has recently been introduced for this purpose, is shown in vertical section in fig. 441. It consists of a wooden chamber divided into parts, over which the endless

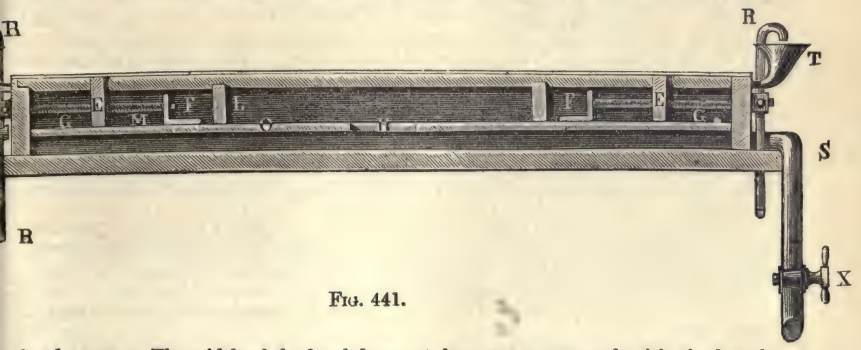


Fig. 441.

band passes. The width of the band does not however correspond with the length of the chamber, but the edges of the cloth run over the partitions (E E) leaving on either side a free space (G G). Into the latter from the pipes (R R) through the funnels (T T) a continual stream of water runs, so as to continually overflow the chambers (G G), and thus form an air-tight water barrier between the gauze band and the transverse divisions (E E), which is essential to prevent outside air gaining admission to the aspiration chamber. A second bottom (O) runs from end to end of the chamber; in the centre of it is a round opening (H) establishing a communication between the upper and lower divisions. From the lower division a pipe (S) runs perpendicularly into a vessel standing about 4 feet lower, and filled with water, below the surface of which the end of the pipe dips. To set the aspirator in action, the lower space is filled with water up to the false bottom (O), the wire-gauze band supporting the paper is brought over the chamber, and the cock (X) is opened. As soon as the water runs off through the pipe (S), a partial vacuum is established in the upper division of the chamber, and this exercises a compressing and absorbing action upon the paper mass.

After the paper has passed the absorption apparatus it is carried, still very moist and soft, between two cylinders covered with felt, where it undergoes pressure. From these cylinders the sheet of paper is carried on an endless band of felt to another pair, constructed of cast iron, hollow, and very smooth, between which it is strongly pressed. It then passes on to a second, but dry, band of felt, and is carried between a third pair of cylinders, but this time the paper is reversed so that the side which had in the previous pressing lain next to the felt is now next to the cylinder. The paper next passes to the drying apparatus, consisting of three hollow iron cylinders heated by steam admitted through their hollow axes; it is carried round these three cylinders in succession, being pressed against the hot surface by an endless band of felt. The second and third drying cylinders have each in connection with them a smooth iron pressing cylinder, by which a final pressing and glazing is imparted to the paper. In some of the newer machines, however, the paper passes between two more pair of polished iron pressing cylinders, by which means a satiny surface is imparted to it. Otherwise it passes from the drying cylinders to the

cutting machine, where it is first slit into strips lengthwise, and then cut transversely into sheets. After the cutting, the sheets are sorted, and defective sheets thrown out, and the finer kinds are submitted to further glazing operations by pressure between polished metal cylinders or between metal plates in a hydraulic press.

Where no size has been added to the paper stuff, or in the case of papers which are required to have a well-sized surface, and therefore have to undergo an *after sizing*, an arrangement for sizing is sometimes worked in connection with the paper making machine. The size is contained in a wooden trough lined with sheet copper, and heated by a jet of steam opening at the bottom of the trough. The paper coming from the drying cylinders is carried round the under surface of a wooden cylinder which dips below the level of the sizing liquid in the trough, then between copper cylinders by which any excess of size is removed, the quantity remaining being regulated by approximation or separation of the cylinders.

Coloured Papers.—Pulp coloured papers are prepared by adding the colouring materials to the paper stuff whilst in the hollander.

Yellow paper is made by adding zinc oxide, ferrous sulphate, decoctions of Campeachy or Pernambuco wood, or umber; but lead chromate is principally used. Payen recommends for 500 parts by weight of dry paper stuff 25 parts of basic lead acetate and 4½ parts of potassium bichromate.

Blue.—For ordinary papers Berlin blue is used, and ultramarine for the finer. Indigo is but little used. A decoction of Campeachy wood with ferrous sulphate and potassium ferrocyanide produces a dark blue paper. Payen gives for 50 parts of paper stuff 2½ parts of ferrous sulphate and 1½ parts of potassium ferrocyanide. But as paper stuff has usually a yellowish tone, which with the blue would give a green shade, to prevent this a little red is added.

Green is almost always prepared by mixing yellow and blue, because the cheaper greens cannot be used on account of their poisonous properties. Lead chromate is used together with Berlin blue or ultramarine. According to Payen 50 parts of paper stuff require 1½ of his yellow, and 3 parts of his blue.

Red is usually coloured with Pernambuco wood, chiefly with an addition of alum, aluminum sulphate, zinc chloride, etc. A more beautiful red is yielded by safflower or carmine, though both these colouring materials are too dear.

Violet is prepared by mixing blue and red, or with extract of logwood.

Rose is prepared by adding 6 parts of extract of Lima wood to 50 parts of dry paper stuff.

Brown is yielded by ochre, umber, or a mixture of chrome yellow and green vitriol, with Pernambuco wood, Berlin blue, etc.

Chamois is obtained, according to Payen, by using 3 parts of double ferrous and cupric sulphate and 3 parts of chloride of lime with 50 parts of paper stuff.

Grey and *black* are produced by means of ferrous sulphate and extract of galls, as well as by mixture of different colouring stuffs in certain proportions; decoction of Campeachy wood with ferric nitrate; also Orleans umber, Berlin blue, lamp black, etc.

In the preparation of ordinary *packing papers* the coloured rags are sometimes assorted and worked up into paper without bleaching, blue paper being obtained from blue rags, brown from brown, etc. Papers made according to this method are called *nature-coloured* or *nature papers*. But the colours never being very fine, they are seldom made.

Surface-coloured paper differs from pulp-coloured paper in not being coloured throughout the body of the paper, but only on the surface, on one or both sides. For this purpose the most insoluble colouring materials, or *body colours* are used, such as ultramarine, Berlin blue, chrome yellow, ochre, etc. The colour is retained upon the surface of the paper by means of a kind of cement, for which purpose ordinary size dissolved in water, or the so-called *alum size* (alum, 1 part; size, 2 parts; water, 10 parts) is generally used. In the preparation of a specially durable surface-paper a second coating of lime and alum is given. Instead of ordinary size gum may be used, but not starch paste, as that would allow the colour to be easily effaced.

The colouring is done either by hand with a brush, or by a colouring machine. In the latter case the paper passes in a long band over a colour cylinder which takes up the colour from the trough beneath, next over an endless gum cloth, and then through several smoothing cylinders provided with brushes, some working longitudinally, and others transversely, by which means the colour is spread equally over the paper. The coloured paper then goes to the drying cylinders, which are heated with steam, and is finally wound on a roller.

Amongst surface papers must also be included *marble paper*, *rainbow*

paper, and paper hangings, each of these being again subdivided according to the pattern.

In the preparation of marble or Turkish paper a very thick mucilage of tragacanth, with a little alum added, is placed in a shallow trough, which at the top is of rather larger dimensions than the sheet of paper to be marbled. Upon this mucilage the marble pattern is formed by sprinkling on it finely triturated colouring materials with a brush. The colours diffuse through the mucilage, running into each other. Into this liquid the paper is carefully laid so as to bring the whole of the surface into contact with it, and then taken out and dried. Granite paper is prepared by sprinkling the different colours one upon another upon the paper by means of brushes. Mottled paper is prepared by sprinkling drops of a dark colour on paper to which the ground colour has been already given. Before the sprinkling the paper is moistened on the reverse side and spread out upon a smooth board; after the sprinkling the board is sloped so as to cause the spots to run.

Rainbow paper is made by using a brush as wide as the paper, and formed of as many separate brushes as the number of bands to be produced. This is dipped carefully into a colour box, which is divided into compartments corresponding with the brush and filled with different coloured pigments, and then passed over the paper so as to produce a number of parallel lines; these are afterwards blended into one another with a second brush. Sometimes the stripes are printed on by means of a mould.

Paper hangings are printed by means of blocks on which the pattern stands in relief. The operation resembles ordinary calico printing.

Gold and silver papers are prepared by laying gold or silver leaf respectively upon paper to which a ground colour, which is reddish-yellow for gold and white for silver, is rubbed up with gum solution; the leaf is either laid upon it whilst it is still moist, or, if it has become perfectly dry, is brushed over with varnish, to which the leaf adheres. After the metal leaf has been laid on, which has to be done carefully to prevent unevenness or flaws, it is pressed down with cotton wool, and the sheet is then glazed and dried.

Usually, in order to impart a shining surface to these papers, they are glazed, satined, or varnished. The glazing is effected by means of a polished stone moving to and fro under the pressure of a spring or a weight. The satining is done by scattering upon the surface fragments of French chalk, and working it with a brush: lastly, a solution of gelatine or of isinglass is used.

Other Kinds of Paper.—Morocco paper is prepared by passing the paper between a bronze cylinder, in which the pattern is engraved, and a cylinder covered with paper. After the embossing is effected a coat of copal or mastic varnish is given to the paper. Damask, shagreen, and other papers are prepared in a similar manner.

Rep or filagree paper can be prepared on the paper machine, by means of a cylinder surrounded by a brass wire work, which is called a dandy roller, placed over the endless band between the absorption chambers and the first pressing cylinders.

The brass wires are separated to correspond with the width of rep required, which is produced in the still soft paper pulp by the pressure of the cylinder.

The water mark can also be given by a similar arrangement, but in this case the cylinder is covered with wire cloth, the design of the water mark (name of the maker, coat of arms, etc.) being worked in relief in fine copper wire. In the production of the water mark in bank notes, paper money, and other valuable papers, where the greatest regularity is required, another method is adopted. The design is worked in brass wire on the inner side of the wire cloth of a hand paper mould. By the settling of the paper stuff there is formed over the raised design a thinner layer of paper fibre than elsewhere, so that the paper at that spot is thinner and more transparent. The difference between the two methods consists in the paper produced by the former being equal throughout as to fibre: the part covered by the design being only compressed together, whilst the transparent water mark in the latter is the result of a thinner layer of paper fibre.

Filter paper has to be made from very carefully purified fibres, which are also specially suited to yield a paper of sufficient strength to sustain in the filter form the pressure of the liquor to be filtered without bursting. With this object linen rags well washed and treated with ley are first submitted to a careful pulping, and then to a not too energetic treatment with chlorine gas; or, better still, chloride of lime. The pulp thus obtained is perfectly freed from adhering lime by means of dilute hydrochloric acid, and afterwards thoroughly washed with very pure water; it is then ready for working into paper.

A grey filter paper, of more spongy properties and filtering more rapidly than the preceding, is obtained by using a mixture of cotton rags and linen. In order to save the fibre it is not specially treated with ley or bleached, but passes from the hollander to the paper mould. Notwithstanding the most careful washing the filter paper obtained from this stuff generally imparts a marked smell to liquids filtered through it.

Berzelius's or Swedish filter paper is characterised by the greatest purity, and is used for especially delicate analysis in chemical laboratories. As a raw material new linen is used, which has been first bleached according to the old method of exposing it kept constantly wet on the ground in the open air. The moist stuff is placed in a reservoir where it undergoes a kind of fermentation, during which a number of pectous and glutinous substances pass into the soluble form; but the process must be carefully watched, as the cellulose itself may easily be attacked. The stuff thus prepared is treated with a strong ley, pulped in the hollander, washed with dilute hydrochloric acid (1 of acid to 10 of water), and finally washed with water until the last trace of acid disappears. It is then worked into paper by hand, and dried without sizing. Most of the fibres of this paper have a length of from $\frac{1}{25}$ to $\frac{1}{8}$ of an inch.

Parchment paper or vegetable parchment is prepared by steeping unsized paper (filter or blotting paper) in slightly diluted sulphuric acid (8 parts of English acid to 1 part of water). The thicker the paper the longer the acid must be allowed to act. Ordinary paper should not lie more than twenty seconds in the acid, because it otherwise becomes brittle. It is then washed with water, next with ammonia, and again with water, to remove the sulphuric acid. A machine for the manufacture of parchment paper has been constructed, in which a band of paper is passed first through sulphuric acid, then through ammonia twice, and afterwards drawn over felt and drying cylinders.

Millboard and Pasteboard.—In the manufacture of millboard, rags that are not suited for ordinary paper, wood stuff, straw stuff, potato skins, beet pressings, and paper refuse, may be used as raw material. The rags are converted in the ordinary hollander into a coarse stuff. In the preliminary preparation of potato skins and beet pressings they are treated with dilute hydrochloric acid at 48° to 50°, then washed again with water and mixed with 1 to 2 per cent. of ammonia. A pectinate of ammonia is thus formed, which gives to the mass a glutinous property. To give it the requisite firmness there is mixed with it 10 per cent. of ordinary paper stuff from rags. Old paper and paper refuse are soaked in water, and allowed to undergo fermentation during fifteen to thirty days, after which they are ground, still wet, between millstones. Generally there is added to stuff to be used for millboard, before moulding, about one-fourth of its weight of clay, chalk, or similar substance.

The ordinary paper moulds are generally used in the same way as for hand paper, the sides of the frame of the mould being, however, higher to hold the necessary thickness of stuff. The couching and pressing between felt is the same as in hand-made paper, after which the boards are dried separately. Ordinary millboard may also be made with a machine, consisting of a cylinder covered with wire gauze, which moves in a trough supplied with pulp. The cylinder becomes coated with a layer of pulp, from which the greater part of the water is removed by a couching cylinder pressing against it; the pulp thus acquires a degree of firmness, and can then be carried on an endless band of felt between the pressing cylinders, after which it is dried, wound, and cut.

A finer fabric, the couched millboard, is made by pressing together freshly drained, but still moist, sheets of paper. It has the advantage over the preceding of being uniform in thickness, it not being possible, in dealing with the quantity of pulp required for a sheet of millboard, to deposit it equally in the mould. Moreover, better materials are used for the couched millboard, such as coarse linen rags, oakum, rope, etc.; straw and wood stuff can also be added.

Pasteboard is made by fixing sheets of finished paper one upon another by means of paste. In this way the finest cardboard, used for playing-cards, etc., is made.

Glazed boards and similar hard substances may be made by the couching method. In this case the stuff must be sized in the vat, and upon the inner side of the mould is laid a sheet of paper made from a long-fibred stuff; also great care is used in the subsequent pressings.

Papier mâché is made by stirring up waste paper or paper refuse to a paste with water and sand, clay, or chalk, removing the greater part of the water by pressure, sizing the mass thus obtained with bone size or paste, and then pressing it into oiled moulds. The moulded object is dried, soaked in linseed oil, and baked. A kind

of papier mâché is also made by pasting separate sheets of paper upon each other in a wooden mould, and subsequently turning the surface in a lathe.

Testing.—Paper which has been sized with animal size can be distinguished from that sized with resin size, as the latter always contains starch, which gives an intensely blue colour when brought into contact with dilute solution or vapour of iodine. The resin may be extracted by treating the paper first with a dilute acid, and then, after drying, with alcohol, which dissolves out the resin set free by the acid; upon evaporation of the alcohol the resin is left as a residue. The amount of animal size used might be estimated by an elementary analysis for nitrogen; the quantity of nitrogen corresponds to about one-fifth of the size. But it is here assumed that the paper consists of vegetable fibre. In unsized paper the quantity of wool or silk fibre present may be ascertained by a nitrogen estimation.

Paper containing an admixture of mineral substances, such as gypsum, heavy spar, lead sulphate, etc.—which has for its object to increase the weight of the paper, but diminishes its firmness—can easily be recognised. If the paper is pure, it should leave only ½ to ¾ per cent of ash; a larger proportion of ash, provided that the water used in the manufacture was not very hard, would indicate an admixture. An admixture of lead sulphate, which may act injuriously if the paper be used for wrapping food in, may be detected by ammonium sulphide, which will give a dark brown spot where the paper is touched with it.

Filter paper should be tested for the amount of ash, that being the best which contains the smallest quantity.

The material used for the blue colouring of a paper may be recognised as follows. Berlin blue is not attacked by acids, whilst it is decolourised by alkalies. Ultramarine is decolourised by acids, with evolution of sulphuretted hydrogen. Cobalt blue is decolourised by either acids or alkalies; its presence may be confirmed by incinerating the paper, and fusing the ash with borax under the blowpipe flame, when cobalt forms a blue glass. Copper may be detected by treating the paper ash with hot hydrochloric acid, and supersaturating the clear filtered solution with ammonia, when if copper be present, a blue colour is produced.

PECTOUS SUBSTANCES.

The substances comprised under this name are generally characterised by the formation of a gelatinous mass or viscous solution when acted upon by heat and dilute acids. The change that takes place in the ripening of fruit is to a great extent due to the modification of which these substances are susceptible.

Pectous substances occur in the intercellular spaces of different plants, and serve the purpose of cementing together parenchymatous cells. In order to see this, it is only necessary to cut a thin slice from the potato, parsnip, beet root, or the epidermal tissues of the cactus. The slices are washed with distilled water so long as the latter takes up soluble matter from them, they are then digested from a fortnight to a month with dilute solution of hydrochloric acid, the whole being kept at a temperature between 15° and 40°, and finally the slices are taken out and washed with pure water. The tissue remains after this treatment quite intact, the individual cells remaining connected together, and connected with the bundle of vessels which cover them, as well as with the epidermal layer. If a little ammonia be added to the water, in a very short time the pectic acid which has been separated from its calcium salt by the action of the hydrochloric acid, dissolves, and the parenchyma cells separate from one another on the slightest touch, while the cuticle and epidermis, as well as the starch-bearing cells, remain entirely unaltered. This experiment proves that the pectous substances occur as intercellular masses.

Pectase.—Together with the pectous substances plants contain a neutral noncrystallisable substance, which resembles diastase in its properties, and has consequently received the name of pectase. It possesses the property of converting a substance, pectose, presently to be described, into pectic and pectosic acids. Pectase occurs in a soluble and insoluble form.

Pectase is dissolved in the juice of turnips, carrots, and other roots, for this juice possesses the property of converting pectin into pectic acid. The flesh of unripe apples contains pectase in the insoluble form, and when reduced to a pulp, and washed with water to remove all the juice, the washed residue is capable of converting pectin into gelatinous pectic acid and pectosic acid.

Soluble pectase is precipitated and rendered insoluble by alcohol. The washed precipitate coagulates pectin, while the supernatant liquid exhibits an indifferent deportment. Aqueous solutions of pectase decompose easily, a mould rapidly forms upon them, and they lose the property of acting upon pectin; their activity is also destroyed by boiling.

Pectous substances are noncrystallisable; many of them, such as pectic acid and pectosic acid, gelatinise and retain in this condition a very large amount of water. This property of gelatinising was the cause of attention being drawn towards these substances; it is also presented by a few other substances, such as gelose and dialose, which in this respect resemble pectous substances.

Pectose.—This substance has not as yet been isolated, but its existence is inferred from the origin of the other pectous compounds—pectin, pectic acid, and pectosic acid —which are supposed to be formed from it.

Pectose occurs in certain roots, such as carrots, turnips, etc., and in most unripe fruits. Under the joint influence of acids and heat it is changed into pectin. In the cold not even concentrated sulphuric acid has any effect upon pectose, a mixture of sulphuric acid and pectose not producing pectin even after standing many days; on the other hand, when pectose is boiled for a short time with water slightly acidulated the change takes place at once. The hardness of unripe fruit is due to pectose, and the softening of fruit when it ripens, or when it is boiled, is owing to the conversion of pectose into pectin.

Pectin.—This substance does not occur in unripe fruit, but is formed when the fruit is boiled, by the action of malic and citric acids upon pectose, also when turnip pulp is boiled with slightly acidulated water. Pectin is most easily prepared from fully ripe fruit, such as juicy pears which are grated, and the juice pressed out and filtered.

The calcium compounds contained in the juice are got rid of by treating the juice with oxalic acid, and the albumin is separated by means of tannin. The clear liquid is then mixed with alcohol, which precipitates pectin as a stringy, doughy mass, which is washed with alcohol, again dissolved in water, and once more precipitated with alcohol, these operations being repeated four or five times, until the liquid when tested ceases to give indications of sugar.

Pectin can be easily obtained from unripe fruit and from roots. The pulp is washed with water, pressed out, stirred up with dilute hydrochloric acid, and the whole then digested for a few days in the cold. Pectin is then precipitated from the expressed liquid by adding alcohol.

The composition of pure pectin may be represented by the formula, $C_{32}H_{40}O_{28}.4H_2O$. It is a colourless noncrystallisable body, soluble in water, and is precipitated by alcohol from its concentrated solutions, in the form of doughy threads, from dilute solutions as a gelatinous mass. Lead acetate gives a precipitate only with parapectin; tribasic lead acetate precipitates pectin completely. The alkaline bases, lime and magnesia, combine with pectin, forming pectates, which are decomposed by acids yielding gelatinous pectic acid. Pectin does not influence a ray of polarised light. When heated with acids pectin is changed into metapectic acid. By the action of pectase it is converted into pectic acid and pectosic acid.

Parapectin.—Pectin when boiled with water, loses its doughy consistency, and is changed into parapectin. The new compound is not crystallisable; it is neutral, and is precipitated from its solutions by alcohol in the form of a transparent jelly. Parapectin may be distinguished from pectin by being precipitated from its solutions by lead acetate. Parapectin dried at a temperature of 100° has the same composition as pectin; at 140° it loses water, and may be represented by the formula, $C_{32}H_{46}O_{31}$; it has then the same composition as in the lead oxide compound. Parapectin when boiled with acids is changed into an acid—parapectic acid, which is precipitable by alcohol, and unites with alkaline bases, forming compounds which are isomeric with the compounds of pectin and parapectin, but are distinguishable from them by yielding a precipitate with barium chloride.

Pectosic Acid.—This acid is insoluble in the presence of acids, and is but slightly soluble in pure cold water; it dissolves, however, in boiling water, and forms a jelly upon cooling. Boiling water converts pectosic acid quickly into pectic acid, the same effect being produced in the cold by pectase, and an excess of alkaline bases.

Pectosic acid is formed by acting upon pectin with cold solutions of potash, soda, or their carbonates, or ammonium carbonate; gelatinous pectosates are thus produced, which yield gelatinous pectosic acids when decomposed with acids. Pectosic acid is also formed when pectase reacts upon a solution of pectin. Pectosic acid is dibasic; its composition may be represented by the formula $C_{32}H_{46}O_{31}$.

Pectic Acid.—This acid occurs abundantly in plants, as a calcium salt forming the intercellular substance of a number of tissues, as in the pith of *Aralia papyrifera*. Pectic acid is also produced by the action of soluble or insoluble pectase upon aqueous solutions of pectin at a temperature of 30°.

Gelatinous pectic acid is insoluble in cold water, and but slightly soluble in boiling water. If it be boiled for a long time, replacing the water that evaporates, it is changed into metapectic acid, a deliquescent and non-gelatinous substance. An excess of caustic alkalies, or their carbonates, transforms pectic acid into the very soluble metapectic acid. The alkaline pectates when treated with acids yield a precipitate of gelatinous pectic acid; when treated with calcium chloride they yield calcium pectate.

Pectic acid is obtained by boiling crushed carrots with a very dilute solution of alkaline carbonate. The pectic acid is in this case formed by the reaction of the alkalies upon pectose. Aqueous solutions of the pectates are precipitated by calcium chloride, and the calcium pectate formed, washed with water, decomposed with hydrochloric acid, yields pectic acid.

Pectic acid, when boiled with alkalies, soon becomes converted into easily soluble metapectic acid.

Pectic acid may be prepared with greater facility as follows: Cactus tissues, that have been previously washed with water, are treated for a few days with dilute hydrochloric acid (1 part acid, 9 parts water). The calcium pectate of the intercellular substance is thus decomposed, and the pure pectic acid remaining may then be washed out from the tissues completely with water without injuring them in the least, and it is only necessary to add to the water 2 or 3 per cent. of ammonia in order to dissolve the pectic acid. The filtered solution decomposed with acid yields pure pectic acid.

Pectic acid is dibasic, and its composition is represented by the formula $C_{32}H_{44}O_{40}$.

It is dissolved by several salts of the alkalies, forming double salts having an acid reaction, which when dissolved in boiling water gelatinise upon cooling.

Parapectic Acid.—This acid is soluble in water; it is not crystallisable. It is formed by prolonged action of boiling water upon pectic acid. The soluble and insoluble pectates are in like manner converted by protracted boiling with water into parapectates.

Parapectic acid has a very acid reaction; it combines with the alkaline bases, forming soluble salts; it is precipitated from its aqueous solutions by excess of baryta; it is dibasic, and is represented by the formula $C_{24}H_{34}O_{23}$.

Metapectic Acid.—This acid, as well as its salts, is easily soluble in water; it is a non-crystallisable acid, precipitable from its solutions by basic lead acetate in presence of ammonia. The metapectates are coloured yellow by an excess of bases; they yield with silver nitrate a white precipitate, which assumes a deep brown colour when boiled with water.

Metapectic acid is formed under several different conditions: 1. Spontaneously in a solution of pectin in the course of a few days; more easily in presence of pectase, the solution becoming sour and then no longer precipitable by alcohol. 2. By the reaction of concentrated acids upon pectin, or by boiling pectin with hydrochloric acid. 3. By the action of potash or soda upon pectin. 4. From pectic acid when suspended in water and left to stand two or three months. 5. Aqueous solutions of parapectic acid pass rapidly into metapectic acid. 6. The pectose of the intercellular substance of various fruits and roots is changed by the action of lime into metapectic acid.

Metapectic acid is also dibasic, and has a constitution represented by the formula $C_{32}H_{56}O_{36}$.

Scheibler prepares metapectic acid by heating mangold-wurzel pulp with milk of lime on a water bath, decomposing the soluble calcium salt with ammonia, and precipitating the solution of the ammonia salt—which must be alkaline—with basic lead acetate. The lead metapectate is then decomposed by sulphuretted hydrogen, the free acid filtered from the lead sulphide, and decolorised by treating it with animal charcoal.

Metapectic acid thus obtained is a colourless liquid with very acid reaction; it decomposes carbonates. Solutions of alkaline metapectates are not precipitated by solutions of lime, baryta, strontia, or copper salts. The acid does not taste sour, although it has a very acid reaction. Metapectic acid, when strongly concentrated, assumes a viscous, almost doughy consistency. Solutions of the acid have the same specific gravity as sugar solutions of the same concentration. Metapectic acid rotates the plane of polarised light more strongly than cane sugar, so that when dextro-rotatory cane sugar and metapectic acid occur together, as is the case in the sugar juice of the factory, 1·6 parts of the cane sugar becomes optically inactive. The rotatory power of neutral or alkaline solutions of metapectates is equal to that of the acid, but alters at once if the acid be heated for a short time with strong inorganic or organic acids. The lævo-rotatory power then diminishes rapidly to zero and passes into the dextro-rotation, which is at its maximum when nearly equal to the original lævo-rotation. Metapectic acid, when treated with acids, undergoes a complete change and then causes a considerable reduction of alkaline solutions of copper. Acids convert metapectic acid into a new organic acid and into a new dextro-rotatory sugar, called pectin sugar. Metapectic acid belongs accordingly to the glucosides.

Pectin Sugar or Pectinose.—This sugar is obtained from metapectic acid that has been altered by heating for some time over the water bath in contact with sulphuric acid. After neutralising with barium carbonate, the barium sulphate is filtered off and the filtrate concentrated by evaporation to a thin syrup, which is then treated with three times its volume of 90 per cent. alcohol, which precipitates the barium salt of the new acid in a flocky condition, while the sugar remains dissolved, but upon evaporating the liquid to a thin syrup soon crystallises out. Pectinose is easily prepared direct from lead metapectate by decomposing this salt with dilute sulphuric acid instead of with sulphuretted hydrogen; after filtration of the lead sulphate a small quantity of sulphuric acid is added, and the whole gently heated over the water bath. The liquid is then treated as above. The first crop of brownish crystals of the sugar are crushed in the mother liquor and spread upon dry bricks. The further purification by recrystallising is much facilitated by this treatment.

Pectin sugar crystallises in long colourless shining prisms.

The crystals are very brittle; they have a pleasant taste, but are not so sweet as cane sugar. Boiling water dissolves large quantities of pectinose, the greater part of which crystallises out upon cooling. Pectinose melts at a gentle heat, but decomposes when the temperature is raised; yielding, like most other kinds of sugar, a very difficultly combustible charcoal. Upon heating with nitric acid pectinose is converted into

oxalic acid without the production of mucic acid. Pectinose dissolves alkaline earths, forming a mucilaginous liquid which becomes yellow upon standing; this liquid is speedily decomposed by heat, behaving in this respect like grape sugar. Its composition is the same as that of grape sugar, $C_{12}H_{24}O_{12}$; in its other properties, however, it is entirely different from grape sugar.

Pectinose does not ferment in contact with yeast.

Pectin, which occurs in much abundance in the juice of ripe fruit, is probably formed during the ripening of fruit by the action of the acids of the fruit upon the pectose existing in unripe fruit; for if the pulp of such unripe fruit be exhausted with water to get rid of all acids, no pectin is produced upon boiling it; pectin is, however, at once formed upon the addition of an acid.

A number of fruit juices after boiling gelatinise upon cooling. These jellies may be formed: 1. By the reaction of pectase upon pectin; pectic acid and pectosic acid being formed. 2. By the solubility of pectic acid in the salts of the alkalies contained in the juice. 3. By a possible decomposition of the pectates by the free acids of the juice. The action of pectase upon pectin may be seen by mixing the juice of currants, which is poor in pectase, with the juice of raspberries, which is especially rich in pectase, and thus produces a jelly with the currant juice.

When imperfectly ripened pears, apples, plums, etc., are slowly heated, different changes take place; the acids of the juice (malic and citric acids) convert the pectose into mucilaginous pectin, part of which is changed by the action of pectase into pectic acid and pectosic acid. Pectase would not be able to effect this change if it were previously coagulated and rendered inactive by rapid heating up to the boiling point. The change of the pectous substances does not extend to the cellulose forming the cell walls; this remains entirely unaltered.

During the early period of growth, in the green state, fruit behaves just like the other green parts of plants, decomposing carbonic dioxide and forming new organic material (tannin, acids, sugar, pectin, and gum). During the second period of actual ripening it behaves in an exactly opposite manner; it no longer assimilates carbonic acid from the air, but on the contrary assimilates oxygen, decomposes a portion of its organic substance, forms carbonic acid, and changes the compounds contained in it in the most various manner. Sugar resists this decomposition the longest.

Gelose.—In the beginning of the year 1856 a Frenchman of the name of De Montravel brought back from his travels a substance consisting of thin white sheets called Chinese moss, and much used by the natives in China in the preparation of edible jellies. This Chinese moss, according to his account, was prepared from lichens growing on certain trees in South China and the Philippines. Payen submitted this substance to examination, and found it to contain 6 per cent. of organic substance soluble in water, as well as a small quantity (0·7 per cent.) of a body soluble in alcohol. The greater part of the insoluble substance swells up in water, forming right-angled prisms. The gelatinous mass dissolves in acetic acid, leaving a nitrogenous residue. When heated with water the gelatinous substance dissolves, leaving the nitrogenous substance and traces of other foreign substances; this solution solidifies upon cooling to a colourless jelly, which contains a quantity of water, equal to about 500 times the weight of the original substance. The gelatinising property of Chinese moss is therefore about ten times as great as that of the best animal gelatine. The jelly when again dried consists of a peculiar body insoluble in dilute alkalies, dilute acids, water, alcohol, ether, and ammonium cuprate. It dissolves in a very small quantity of concentrated sulphuric acid, or hydrochloric acid, assuming a brown colour; the solution solidifies after a time to a mass insoluble in water and alkalies.

Gelose has the following percentage composition:—

Carbon	42·770
Hydrogen	5·775
Oxygen	51·455

Up to the present time no compound of gelose has been prepared from which the chemical constitution of gelose might be ascertained. According to recent reports of Champion, the riband-like strips of the substance are prepared by pouring the jelly forming liquid into a shallow vessel, allowing it to solidify, and then cutting it into even prisms, which upon drying shrink up considerably, forming a riband-like mass. The same traveller brought with him specimens of the plant from which the moss is prepared. According to Decaisne, it is an alga, *Grateloupia filicina*.

Gelose has a general importance, inasmuch as it can be used with advantage in the preparation of edible jellies. It has this advantage over ordinary gelatine and isinglass, that it is entirely odourless and very durable.

Attempts made to prepare gelose from different kinds of lichens have been hitherto

unsuccessful. Payen, however, succeeded in proving the presence of gelose in large quantities in two marine algæ, *Gelidium corneum* from Java, and *Plocaria lichenoides* from the Mauritius.

Gelidium corneum was treated successively with cold dilute hydrochloric acid (2 per cent.), water, and ammonia; and again washed, owing to the extraction of different salts and organic substances, it lost 53 per cent. in weight. After boiling the residue with water, all the tissues appeared unaltered, and it yielded a liquid which upon solidifying formed a colourless transparent jelly, which was proved to be identical with gelose.

Cubilose, Dialose, Apiin.—To substances possessing the property of gelatinising, and therefore resembling those just described, belong the three bodies, cubilose, dialose, and apiin. The first, cubilose, is the chief constituent of the East India birds' nests. Many opinions have been expressed concerning its origin, some considering it to be a product of vegetable, others one of animal origin. According to the latest researches of Payen, it appears to be a kind of slime excreted by certain birds during the pairing period.

Dialose has been found by Payen in the fruit of a species of *Dialium*, which is used in China for washing instead of soap. Apiin is a gelatinous substance, discovered by Braconnot, and obtained by extraction of parsley (*Apium petroselinum*), its composition being represented by the formula $C_{24}H_{14}O_{13}$.

ALBUMINOUS SUBSTANCES.

The various substances which resemble the albumin of eggs and blood occur both in plants and animals; they all contain nitrogen, and from a chemical point of view present analogies which indicate that their constitution is referable to a common type. In the natural state albuminous substances are always combined with water in a colloid condition, which cannot be separated by squeezing, but only under conditions similar to those by which hydrated crystals lose water.

In its best known form albumin occurs as white of egg, and as the chief constituent of the serum of blood. Other forms of albumin occur in the juices of plants.

Fibrin forms the mass of muscular tissue, and gluten or vegetable fibrin occurs in the grain of wheat. Fibroin is an analogous substance, constituting about 16 per cent. of raw silk. Casein occurs in milk. Legumin is the name given to the albuminous substance found in the seeds of leguminous plants, such as beans, peas, and lentils.

Globulin or crystallin is an albuminous principle occurring in the crystalline lens, while vitellin is the designation of the albuminoid constituent of egg-yelks.

Syntonin is an albuminous substance derived from muscle-fibrin by treatment with dilute hydrochloric acid and precipitation of the solution with ammonia.

Gelatin and chondrin are substances obtained from bone, cartilage and certain other animal tissues; sericin is an analogous constituent of raw silk.

The composition of various albuminoid substances is shown by the following table:—

	Albumin	Mucin	Gelatin	Chondrin	Fibrin	Syntonin	Lardacein
	Mulder	—	—	Mulder	Mulder	—	—
C.	53·5	52·4	50·16	49·97	52·7	54·1	53·6
H.	7·0	7·0	6·60	6·63	6·9	7·2	7·0
N.	15·5	12·8	18·30	14·44	15·4	16·1	15·0
S.	1·6	Nil	0·14	·38	1·2	1·1	1·3
O.	22·0	27·8	24·80	28·58	23·5	21·5	23·1

	Protein	Casein	Globulin	Vitellin	Legumin
	Mulder	Mulder	Mulder	Gobley	Dumas and Cahours
C.	53·7	53·85	54·5	52·26	18·1
H.	7·0	7·15	6·9	7·25	6·91
N.	14·2	15·65	16.5	15·06	50·53
S.	1·6	0·85	22·1	1·17	24·41
O.	23·5	22·52		23·24	
P.	—	—	—	1·02	—

It will be seen that Gobley found a small percentage of phosphorus in vitellin, and other observers have testified to the presence of phosphorus in other substances considered to be albuminous; nevertheless, phosphorus is no a normal constituent of any form of albumin, and where it has been found it is to be regarded solely as an impurity derived from the association of a trace of some phosphorised substance such as lecithin. Thus the yelk of egg contains a great deal of lecithin, and the substance of brain, as shown by Thudichum and others, is largely composed of this and allied phosphorised principles, whose constitution is now well established. Sulphur

is not a constant constituent, and, indeed, there is some little doubt whether it really forms part of the albumin molecule, or whether it is only present by accident. However this may be, it admits of removal in many cases, as, for instance, by digestion with alkalies. The compound thus formed, termed alkali-albuminate, is free from sulphur. Albumin has a very high molecular weight, which has been approximately determined as 1612 by two methods, namely, by analyses of the potassic and platino-hydrocyanic combinations.

Regarding sulphur as an essential constituent of albuminoids, Lieberkuhn proposed for them the formula $C_{72}H_{112}N_{18}SO_{22}$; this formula, however, must only be accepted provisionally.

All albuminous substances give up their sulphur to alkalies, forming sulphide and hyposulphite and soluble alkali-albuminate, which, on neutralisation with an acid, yields a substance which Mulder termed protein, and regarded as the base of all albuminous substances. It has, however, been shown since then, that protein still contains sulphur in some instances, in a form not removable by alkalies.

Liebig viewed albuminoid substances as being isomeric, while Sterry-Hunt considered them to be amides or nitrites of cellulose, dextrin, gum, or sugar. This latter theory is not consistent with facts to be stated hereafter.

Berthelot viewed the substances under description as complex amides.

Strecker viewed them as composed of a great number of radicles, most of which are common to all forms, while a few are peculiar to each form; he thus accounted for the differences to be observed in the properties of albumin in its various states.

Thus, for instance, Thudichum and Kingzett have recently shown that all the various phosphorised substances derived from the brain, from yelk of eggs, or from blood-corpuscles, etc., are constructed on a common type. When decomposed by boiling with baryta water, dilute acids, or other hydrating agents, the phosphorus they contain is invariably yielded as phosphoglyceric acid ($C_3H_9PO_6$); the nitrogen is always yielded in the form of neurine, oxyneurine, or choline ($C_5H_{15}NO_2$). The only other products of decomposition are various fatty acids, and the sums of the decomposition products give the same formulæ as those obtained by analysis of various compounds of these principles themselves. The constitution of these bodies appears therefore to be representable by a common formula, which is that of glycerine having two hydroxyls replaced by fat acid radicles, and the third by phosphoryl; one of the hydroxyls of the phosphoryl is in its turn replaced by the nitrogenised nucleus. Thus, the formula for lecithin is

$$C_3H_5\begin{cases}C_{18}H_{33}O_2\\C_{16}H_{31}O_2\\(HO)\,OPO\,(C_5H_{15}NO_2)\end{cases} = C_{42}H_{85}NPO_9.$$

The general structure of all similar bodies is exhibited by glycerophosphoric acid as a type:

$$C_3H_5\begin{cases}HO\\HO\\HO\,(OPO)\,(HO).\end{cases}$$

As albumin occurs in nature it is generally associated with mineral salts; and from the difficulty experienced in ridding it entirely of these, and from other considerations, it is not improbable that the molecule of albumin has a feeble power of combination with salts, just as alkaloids have. In fact, the products of decomposition of albuminous substances support this view. In the blood and all serous liquids, and in the juices of vegetables and plants, the albumin exists in a liquid state, and on boiling the albuminous liquids the albumin is precipitated in a coagulated state. It is necessary in such cases to have the solution as nearly as possible neutral, or coagulation does not invariably occur.

Albumin exists in two states, namely soluble and insoluble, and the second of these may be readily produced from the first named, although the immediate causes underlying the transformation are unknown. If the serum of blood be evaporated below 40° C. the product is soluble in water, but if a higher temperature be applied, the product is insoluble in water. Again, if a dilute solution of white of egg be boiled, the albumin is thrown down in an insoluble condition; or if serum of blood be submitted to a current of air in the presence of turpentine at normal temperatures, peroxide of hydrogen is formed, and this bleaches the solution, which then yields on evaporation at a gentle temperature insoluble albumin.

Albuminous solutions are precipitated by nitric acid, strong alcohol, corrosive sublimate, phenol, tannic acid, etc.

Coagulated albumin, like fibrin, dissolves in concentrated hydrochloric acid, especially with the aid of heat, forming a blue or violet solution, which examined spectroscopically shows an absorption band in the yellow-green. Coagulated albumin

also dissolves in strong nitric acid, giving a yellow solution, and when a small quantity of mercurous nitrate is added and the mixture boiled, a crimson precipitate is produced.

Albumin solutions grow opalescent at 66° C., and at 80° C. they coagulate.

Fibrin may be obtained by whipping blood, during which operation it adheres to the twigs used, in the form of threads. When placed in peroxide of hydrogen, it causes the evolution of oxygen.

Albumin derived from white of egg is designated **ovalbumin**; and that from serum of blood is termed **seralbumin**.

White of egg when heated in a sealed tube at 150° to 200° C., passes first into an opaque coagulum, which is afterwards transformed into a reddish transparent jelly, and finally into a reddish liquid, behaving with reagents like ordinary solutions of albumin, but not coagulable by heat. When white of egg is placed in a dialyser over solutions of acids, there are formed upon the dialyser what G. S. Johnson regards as compounds of albumin. The figures he obtained from a determination of the acid contained in the presumed compounds, lead to the following formulæ for them, if Lieberkuhn's formula for albumin be accepted:—

$C_{72}H_{112}N_{18}SO_{22}\cdot 2HNO_3$
$C_{72}H_{112}N_{18}SO_{22}\cdot 2HCl$
$C_{72}H_{112}N_{18}SO_{22}\cdot H_2SO_4$
$2(C_{72}H_{112}N_{18}SO_{22})\cdot 3H_3PO_4$
$C_{72}H_{112}N_{18}SO_{22}\cdot HPO_3$
$C_{72}H_{112}N_{18}SO_{22}\cdot 2H_3C_6H_5O_7$
$C_{72}H_{112}N_{18}SO_{22}\cdot H_2C_2O_4$
$C_{72}H_{112}N_{18}SO_{22}\cdot 2H_2C_4O_6$
$C_{72}H_{112}N_{18}SO_{22}\cdot HC_2H_3O_2$.

Although the existence of such definite compounds had been long before rendered almost certain by the investigations of Lieberkuhn and others, further investigation and the ultimate analyses of the substances are to be desired, before the formulæ assigned to them can be accepted.

In addition to these acid compounds, a number of albuminates have been described, although the following formulæ assigned to them are to a certain extent hypothetical:—

Albuminate of Barium, $C_{72}H_{110}BaN_{18}SO_{22} + H_2O$ (?)
„ „ Copper, $C_{72}H_{110}CuN_{18}SO_{22} + H_2O$ (?)
„ „ Potassium, $C_{72}H_{110}K_2N_{18}SO_{22} + H_2O$ (?)
„ „ Sodium, $C_{72}H_{110}Na_2N_{18}SO_{22}$ (?)
„ „ Silver, $C_{72}H_{110}Ag_2N_{18}SO_{22} + H_2O$ (?)
„ „ Zinc, $C_{72}H_{110}Zn_2N_{18}SO_{22} + H_2O$ (?)

besides the albuminates of lead and mercury.

When albuminoid substances are submitted to the gradual oxidising action of a mixture of potassic dichromate and sulphuric acid, or a mixture of manganic dioxide and sulphuric acid, various products are obtained. Guckelberger and Schlieper have both found, among the products of oxidation, the following:—

Formic acid	Acetic aldehyde	Benzoic acid.
Acetic „	Propionic „	Benzoyl hydride.
Propionic „	Butyric „	Hydrocyanic acid.
Butyric „		Valeronitrite.
Valeric „		
Caproic „		

Béchamp, during the oxidation of albumin by means of potassic permanganate, observed the presence of a small quantity of urea, a matter of extreme importance when considered in the light of the more recent researches of Schützenberger.

In 1820, Braconnot obtained glycocine or sugar of gelatin (amido-acetic acid) by boiling gelatin with dilute sulphuric acid, and when muscle was heated in a similar manner he obtained leucine $C_6H_{13}NO_2$ (amido-caproic acid). Liebig demonstrated the formation of an accompanying crystalline body, namely, tyrosine $C_9H_{11}NO_3$ (oxyphenyl-amido-propionic acid). Erlenmeyer and Schaeffer continued these researches and obtained for 100 parts of dry substance—

	Leucine	Tyrosine
Fibrin	14	0·8
Albumin	10	1·0
Syntonin	18	1·0

Ritthausen obtained from products formed by the action of boiling dilute sulphuric acid on vegetable nitrogenous substances, two crystallisable acids: glucamic acid $C_5H_9NO_4$ from coaglutin, and legumic acid $C_8H_{14}N_2O_6$ from legumin.

Schützenberger commenced his researches with the idea that the urea group exists in albumin, and although he has not succeeded in isolating this substance, he has at least obtained evidence of its existence. His method consists in boiling albumin during a number of hours with a solution of caustic baryta, a process which of course destroys any urea that might be formed. Nevertheless, he has obtained carbonic acid and ammonia in the exact proportions which urea would yield, and he concludes that out of the eighteen atoms of nitrogen in the molecule of albumin, four belong to the urea group.

Besides urea and tyrosine, traces of sulphurous acid and sulphuretted hydrogen are formed, and oxalic and acetic acids. These substances are accompanied by the amido-acids of the series $C_nH_{2n+1}NO_2$, corresponding to the fat acids $C_nH_{2n}O_2$, from amido-œnanthylic acid $C_7H_{15}NO_2$, to amido-propionic acid; leucine $C_6H_{13}NO_2$; butalinine $C_5H_{11}NO_2$; and amido-butyric acid $C_4H_9NO_2$. Besides these, one or two acids allied to aspartic acid $C_5H_9NO_4$, and glutamic acid $C_4H_7NO_4$, are produced, and one or two analogous to legumic acid $C_8H_{14}N_2O_6$. Schützenberger also obtained by decomposition of albumen with baryta, a small quantity of a dextrin-like body which was resolved by boiling in acids into a substance like sugar. From his researches he regards the albuminoids as urea and amido-acid combinations.

It should be observed that when albumin is subjected to the influence of caustic alkalies melted in their water of crystallisation there are obtained just those products which might be expected from a further action upon the substances yielded by the baryta process.

Thudichum obtained several alkaloids from the baryta decomposition of albumin, and among them one of the formula $C_3H_6NO_5$.

The importance of the results here briefly described will be seen when it is considered that the putrefaction of albuminoid substances gives rise to the production of leucine, tyrosine, and a number of volatile fat acids of the series $C_nH_{2n}O_2$, ammonia, and a number of compound ammonias, carbonic dioxide, sulphuretted hydrogen, hydrogen and nitrogen.

It is known that in the presence of putrefied fibrin, leucine is resolved into ammonia and valerianic acid, and from all that is known the products observed during putrefaction are those of hydratation modified according to circumstances, especially by contact with special ferments or by the presence of air.

By the further prosecution of such investigations as those described, it may be possible to hope for something like a true explanation of the action of antiseptics and disinfectants; for the power of an antiseptic is undoubtedly one which confers upon the molecule of albumin increased stability, thus rendering the attacks of so-called germs or ferments of less avail in splitting up the molecule, and therefore rendering them powerless to reproduce themselves and cause simultaneously putrefaction and disease.

Uses of Albumin.—Albumin occurs in commerce in several forms, differing in purity and whiteness.

White of egg contains 12 per cent. of albumin, and for commercial purposes this is dissolved in water and evaporated in thin films at a gentle temperature (40° C.), thus forming white scales, which before use have to be dissolved in water again. Egg albumin is used by calico printers for fixing the better and lighter sorts of colours; it is also used for photographic purposes on account of its whiteness compared with seralbumin. Blood contains about 7 per cent. of albumin, and it is from this source that most of the albumin used in the arts is made. The blood of slaughtered animals is allowed to stand in shallow vessels until the fibrin has coagulated; during this spontaneous process most of the colouring matter of the blood is enveloped in the fibrinous clot, and the serum is drawn off and evaporated down at a gentle temperature.

An inferior sort of blood albumin is prepared by beating or shaking blood in vessels provided with staves; in this way the fibrin is coagulated, but most of the blood corpuscles remain in the serum; hence albumin prepared by this process is not so good, and can only be used for fixing the darker colours on calico, etc.

Albumin in a state of solution is also used for clarifying vinous and syrupy liquids, inasmuch as when boiled with them it coagulates and envelopes the substances which it is desired to remove. Thus it is used to a considerable extent in sugar refining.

For the better purposes, as already stated, it is necessary to use egg albumin, and this is not only scarce, but its use withdraws a large amount of food from the market. Moreover on account of the liability of albuminous solutions to decomposition, albumin is only met with in commerce in the dry state. Thus, there is the trouble of redissolving the albumin for use, and, since the whole does not redissolve, there is always some loss.

Having regard to these facts Messrs. Kingzett and Zingler have recently introduced a method which consists in subjecting serum for several hours to a current of air at about 30–40° C. in the presence of about 10 per cent. turpentine. In this way peroxide of hydrogen and camphoric acid are produced by the oxidation of the turpentine. The former of these substances, by its oxidising action, bleaches the serum at once, while the camphoric acid exercises an antiseptic action, so that the albumin may be kept indefinitely in the state of solution. Albumin thus prepared admits of the fixing of some colours which could not before be made fast. As thus prepared the albumin solution contains about 17 oz. to the gallon.

GELATIN, ISINGLASS, GLUE, AND SIZE.

Gelatin is a nitrogenous substance of the albuminous class, and is obtained from white fibrous tissue, cellular tissue, skin, serous membranes, bones and other animal tissues.

It may be prepared by various methods, of which the following will serve as illustrations.

According to Nelson's patent method, the parings, etc. of skins, are washed, their surfaces scored, and then digested in a dilute caustic ley (soda) during about 10 days. After this they are removed to an air-tight vat lined with cement, and kept at a temperature of 21°, after which they are exposed to a current of sulphurous oxide in a wooden chamber. The moisture is next expelled by pressure, and the product heated with fresh water in earthen vessels provided with a steam jacket. In this way soluble gelatin is prepared and may be purified by straining it at a temperature of 38° to 49°.

From bones this substance is prepared by the combined action of steam and a current of water which is allowed to trickle over the broken fragments in a suitable apparatus. Calf's-foot jelly is an alimentary article consisting of gelatin, while isinglass contains from 86 to 93 per cent. of gelatin, and is prepared from the inner membrane of the floating bladder of sturgeons and other fish.

By another process the phosphates of calcium contained in bones are dissolved out by dilute hydrochloric acid or sulphuric acid, and the gelatinous residue, on boiling with water under pressure, furnishes a kind of soup which is said to be nutritious and has been used in foreign hospitals, etc.

From time to time a number of modifications have been introduced into the preparation of commercial gelatin with the view of improving its hardness and sizing qualities.

This manufacture of gelatin from the skins of animals gives rise to another branch of industry of some importance, namely, the manufacture of glue and size. Glue, in fact, is the crude solid form of gelatin, whilst size is a semi-liquid state of the same substance.

The strongest glue is furnished by the parings of ox hides; the ears and refuse trimmings of thick hides yield on an average 45 to 50 per cent. glue.

The process to which these clippings are subjected may be briefly described as follows.

They are first steeped in lime water, to remove the air and blood, and after washing in cold water, are exposed in layers to the air, so that whatever lime is left in the tissues may be converted into carbonate. After this, the dippings are boiled in water contained in a large copper, sometimes being first enclosed in a coarse cloth to prevent the adhesion and consequent burning of any gelatin upon the bottom of the vessel. It is, however, preferred to boil the mixture under moderate pressure, and this operation is continued until it is found that the liquor contains so much dissolved substance that it gelatinises on cooling, when it is run into a deep vessel and maintained in a warm state to allow of the deposition of impurities, etc. Any animal substance left undissolved gives, on a second boiling, an inferior kind of glue, and if there be any third quantity it constitutes a sort of size; the ultimate residue is useful as manure. The solution after settling is run into wooden boxes, where it cools, and gelatinises, and the solid mass is cut up into blocks, and finally into slices, which are dried by exposing them to a free current of air upon nets placed in a wooden frame. Much of the success of this operation depends upon atmospheric conditions; if the weather be hot, there is a danger of the whole liquefying; in foggy weather the glue is apt to turn mouldy, and frost has a tendency to make it crack into fragments. Spring and autumn are therefore the most favourable seasons for the performance of the drying operation. Artificial drying now commonly resorted to, and this obviates the difficulties above enumerated.

Properly-made glue is a hard, brittle, pale-brown, glassy-looking substance, which swells up, but does not dissolve in cold water.

Size is usually made from the thinner kinds of skins and is chiefly used in the gelatinous condition.

THE MANUFACTURE OF LEATHER.

Ox hides are imported from the plains of South America and the Cape of Good Hope, and the leather prepared from them is chiefly used for making soles of boots and shoes, for harness, and articles in which strength and durability are the requisite qualities.

Calves' and seals' skins furnish leather for the uppers of boots and shoes, while for book-binding and more general articles, sheep skins constitute the chief material used.

Some hides are immensely thick; for instance, that of the hippopotamus is often as much as two inches in thickness.

They may be used either as they come from the animals, or after being preserved, an operation which is necessary when the hides come from abroad. This preservation is generally carried out by soaking the skins in a strong solution of salt, but various agents are now employed for the same purpose.

In all cases where it is intended to make leather, the first thing necessary is to cleanse the skins thoroughly from any preservative agent that may have been used, blood, and other matters. This is done by washing or immersion in pits containing frequently renewed water. To expedite this operation the hides are often sent to the fulling mills, where they are beaten with heavy hammers shod with iron, and in this way they are also rendered supple. After trimming, the hides are then freed from fatty matters and the hair loosened by means of lime water or a weak solution of caustic soda. In other places the hides are exposed in a warm room until putrefaction begins, and in this way the hair becomes loosened just as readily as lime or soda effects it.

To remove the hair, the hides are next placed upon tables termed 'beams,' and while stretched out, the operator shaves the skin by means of a two-handled knife which is worked over the surface.

Rinsing is then resorted to, after which the hides are immersed for a number of hours in a very dilute bath of sulphuric acid; this removes the lime or soda, makes the skins swell, and indeed fits them for the tanning process, which is of an extremely slow nature.

During a period of about six weeks the hides are passed through a series of wooden-lined pits containing an infusion of oak-bark termed ooze, of gradually increasing strength, and are finally placed in other pits in an extended state, one above the other, with layers of powdered oak bark between each; these pits are then filled up with water, and in this state the hides stay for three months. This last operation is usually repeated a second time or even a third time, until the whole texture is tanned throughout; this is evidenced by the uniform brown colour which obtains. This tanning is effected by the combination of the vegetable astringent principles of the oak bark with the skins, and when completed the hides are dried in lofts fed with a good current of air, and generally warmed by steam pipes; after this the hides have to be beaten and rolled.

In the tanning process above described, it is the tannic acid of the oak bark which by its combination with the gelatinous tissue of the hides, produces the substance called leather. Other substances are often used, but generally in combination with oak-bark. Thus *sumach* from the bark of Rhus cotinus, or Rhus coriaria; *catechu* or Terra Japonica which is furnished by various species of acacia; *dividivi*, the crushed pods of Cæsalpinia coriaria; *mimosa* from the bark and pods of several kinds of Prosopis; *valonia*, the acorn of the prickly-cupped oak (Quercus Ægelops); and *nut-galls*, are all used.

In the process called *Tawing*, which is only applied to the thinner kinds of hides, such as those of sheep, goats, and calves, alum and common salt are used, and are worked with some oily matter into the skins. The process termed *Shamoying* consists essentially in combining with the softer part of the hides of the goat, doe, or chamois, some suitable fatty matter.

Light kinds of parchment are prepared from calf or sheep skins, by the use of lime, while the stronger kinds are made from the skins of asses and pigs.

Altogether, the processes used in the preparation of leather differ according to the nature of the skin, and the kind of leather it is proposed to make, and the description here given is but an outline of some of the most important methods in use.

FAT AND OIL.

Both fat and oil occur as constituents of animals as well as of plants. Substances of this class are found in all parts of plants, especially in seeds and in many kinds of fruit; whilst in animals they are often deposited in large quantities in particular tissues.

Characters.—The various kinds of fat occurring in vegetables and animals are distinguished as well by their physical as by their chemical characters. The state of aggregation is at once a distinctive feature, and many kinds of fat may be thus distinguished. Such as are liquid at the ordinary temperature are termed fat oils; whilst those which have a soft consistency at the ordinary temperature and melt at about 30° are classified with butter or lard. Those kinds of fat which melt at higher temperatures and are solid at the normal temperature are termed tallow. Most kinds of fat are liquid at the ordinary temperature, or a little above it. In a fresh condition they are white or colourless, or sometimes faintly yellow; they possess but a slight smell, and have an average specific gravity of 0·9. They are insoluble in water, but form with it or with mucilage an emulsion; they dissolve with difficulty in alcohol, freely in ether, in carbon bisulphide, in turpentine and in other volatile oils. Most of them leave a greasy stain upon linen and paper, thus presenting a marked distinction from ethereal oils, which volatilise completely; but some fat oils dry up in the air (by absorption of oxygen) to such an extent that no greasy stain is left upon the paper. These latter are termed drying oils.

Heated to 250 or 300°, the fats are decomposed, yielding free volatile acids and products of disagreeable odour, viz., acrolein, allylic alcohol, water, etc., leaving a carbonaceous residue; when heated in sealed vessels to a red heat they are converted almost entirely, with separation of carbon, into combustible gas consisting of marsh gas, olefiant gas, acetylene, carbonic oxide and carbonic anhydride. Most fats absorb oxygen from the atmosphere, becoming viscid and acquiring a sharp rancid smell. As oxygen is absorbed, heat is generated, and if this takes place rapidly the mass may take fire, especially when porous bodies like wool, cotton, etc., saturated with the fatty oils are exposed in such a manner as to present a large surface to the air, thus giving rise to the danger of spontaneous combustion; great care, therefore, is required where such material accumulates, as in turkey-red dye works or in storing greasy rags from machinery use.

Composition.—The different kinds of fat must be regarded as acid ethers of the tri-atomic alcohol, glycerin, the composition of which is represented by the formula $\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$. By replacing the typical hydrogen with acid radicles, glycerides or fats are formed. Stearin consequently is represented by the formula $\left.\begin{matrix}C_3H_5\\3C_{18}H_{35}O\end{matrix}\right\}O_3$, or glyceryl stearate. The term fatty acids is applied to the great number of like acids forming fats with glycerin.

Stearic Acid $\left.\begin{matrix}C_{18}H_{35}O\\H\end{matrix}\right\}O$ forms a chief constituent of hard fats. In a pure state it is white and crystalline, insoluble in hot and in cold water, but soluble in alcohol. It melts at 69·9° and forms salts with bases. The alkaline stearates are soluble in water, the ammonium salt particularly so. The potash or soda salts are separated from their solutions by an excess of alkali, or by sodic chloride. On this latter property depends the separation of soap—chiefly an alkaline stearate—by mixing the soap ley with common salt (sodic chloride). When a concentrated solution of an alkaline stearate is mixed with much water, a turbidity ensues, due to the precipitation of a stearic acid compound with but little alkali; the rest of the alkali and a small quantity of stearic acid remain dissolved. The stearates of the alkaline earths (lime, baryta, strontia, magnesia), are insoluble in water, consequently when lime or baryta water is added to a soap solution, a calcium or barium salt of the fatty acid is precipitated. It is for this reason that hard waters, or waters rich in

lime salts, are not suitable for washing purposes; the stearates of the heavy metals are also insoluble in water.

Palmitic Acid $\left.\begin{matrix}C_{16}H_{31}O\\H\end{matrix}\right\}O$.—This acid resembles stearic acid in its chemical properties. At ordinary temperatures it is hard and crystalline, insoluble in water but soluble in alcohol; with bases it forms soluble and insoluble salts. It occurs in nearly all fats, but in less quantity than stearic acid; margaric acid $C_{17}H_{34}O_2$, whose existence has been disputed, theoretically ranks between stearic and palmitic acids.

Oleic Acid $\left.\begin{matrix}C_{18}H_{33}O\\H\end{matrix}\right\}O$ is liquid at ordinary temperatures, solidifies at +4°, and then melts at +14°. It is insoluble in water, but easily soluble in alcohol, in ether, and in carbon bisulphide. The solid acid undergoes no change when exposed to the air, the liquid acid is assumed to absorb oxygen rapidly, and to be transformed into several oxidised products. The acid so changed remains liquid even below 0°, and possesses a rancid odour and taste. By distillation, the acid is decomposed into several gaseous and liquid products, amongst which is sebacic acid, whilst charcoal remains behind.

Nitric acid converts oleic acid into suberic acid, pimelic acid, etc., with a great number of very volatile acids including acetic, butyric, valeric, caproic, and capric acids. In general the oleates resemble the stearates and palmitates. Potassic oleate is soft, attracts water readily, dissolves in 2 or 3 parts of water, but is less easily decomposed by water than the corresponding stearate and palmitate. Sodic and potassic chloride, and other soluble salts separate alkaline oleates from their aqueous solutions. Sodic oleate is harder than the potassium salt, less deliquescent, and more difficultly soluble. The remaining salts are insoluble in water, soluble in alcohol, and in oils, and fusible by gentle heat. Plumbic oleate is the basis of the ordinary lead plaster. Nitrous acid in the cold transforms oleic acid into a solid isomer, elaïdic acid, which crystallises from alcohol in splendid white laminæ, having the same composition as oleic acid, but with a melting point of 45°.

The various fats comprise a great number of acids belonging to the same homologous series as stearic acid, differing only in their composition by the group CH_2 or a multiple thereof. Although the series of this group is incomplete, yet very many, as butyric, valeric, caproic, and œnanthylic acids are found in the various kinds of fats, and this series, beginning with formic acid (CH_2O_2) and ending with melissic acid $C_{30}H_{60}O_2$, forms the so-called 'fat acid' series.

Behaviour of Fats towards Basic Substances.—When fats are heated with strong bases such as potash, soda, baryta, lime, etc., in the presence of water, they are decomposed, yielding glycerin and soaps or combinations of the fatty acids with the base. The term saponification or plastering, originally used to express the process of soap and plaster making, is now extended to these reactions. The following equation expresses the saponification of glyceryl oleate or olein with caustic potash, and serves to illustrate the saponification of fats generally:

$$\left.\begin{matrix}C_3H_5\\3C_{18}H_{33}O\end{matrix}\right\}O_3 + 3KHO = 3\left(\left.\begin{matrix}C_{18}H_{33}O\\K\end{matrix}\right\}O\right) + \left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$$

Sulphuric acid decomposes fatty bodies in such a manner that by the addition of water they split up into the respective fat acid and glycerin: it is evident, therefore, that the action of the acid differs but slightly from the change produced by saponification. A recent process, wherein fat is decomposed by superheated steam into glycerin and fat acid, is being largely used in the manufacture of stearic acid. The change is thus expressed:

$$\left.\begin{matrix}C_3H_5\\3C_{18}C_{35}O\end{matrix}\right\}O_3 + 3OH_2 = 3\left(\left.\begin{matrix}C_{18}H_{35}O\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$$

Stearin or Glyceryl Stearate $\left.\begin{matrix}C_3H_5\\3C_{18}H_{35}O\end{matrix}\right\}O_3$ is found in animal fat generally, but chiefly in beef and mutton fat: the presence of stearin increases their consistency. To prepare it pure, melted tallow is recrystallised several times from ether or turpentine. So prepared it is white and crystalline, insoluble in water, difficultly soluble in hot alcohol, but easily soluble in ether. From the fact that the melting point ranges from 55° to 71° C., its permanent point (as deduced by the observations of Heintz), there appear to exist several modifications of stearin, and Duffy has confirmed this presumption by the description of a modification which melts at 63°.

Palmitin, $\left.\begin{matrix}C_3H_5\\3C_{16}H_{31}O\end{matrix}\right\}O_3$ is found in most fats and can be obtained from palm oil by strong pressure; then by treating the residue with boiling alcohol and recrystal-

lising it several times from ether, it is obtained white and crystalline, soluble with difficulty in boiling alcohol, but easily soluble in ether. Its melting point is 60° and solidifying point 46°.

Olein $\left.\begin{matrix} C_3H_5 \\ 3C_{18}H_{33}O \end{matrix}\right\}O_3$ is the chief constituent of the liquid non-drying oils, but is also found in many fats of the animal and vegetable kingdoms, as for instance mutton and beef fats and palm oil. In order to separate it from the other fats, the mixture is gently warmed with concentrated potash ley, whereby only stearin, etc., becomes saponified, allowing the olein which floats on the alkaline liquid to be mechanically separated. It is colourless, liquid below 0°; and it is less easily saponified than the other glycerides, but oxidises much more quickly in the air. By acting on olein with nitric acid, elaïdin is produced. All the glycerides can be artificially prepared.

Tallow.—Tallow consists chiefly of stearin mixed with palmitin and olein. It is solid at 12° to 15°, but its degree of solidity depends upon several conditions, such as the kind of animal it is obtained from, upon the feed of the animal, etc. It is also to be noticed that fat produced in summer is softer than winter fat. The fat occurs enveloped in very thin cellular tissues composed of nitrogenous compounds, and in fresh marrow the globular cells can be easily separated and distinctly recognised under the microscope. In consequence of moist membrane and other easily decomposed substances being mingled with the fat, it readily undergoes change in the air, therefore it is necessary, especially in summer, either to keep it in a cool and airy place, or at once to separate it from the membranes by melting.

Tallow melting.—The tallow is first cut up and hacked into pieces by knives, in order to facilitate the melting out of the fat from the cells. The finely-divided tallow is placed in a copper or brass vessel, and is heated, either over an open fire, or by means of steam, which is better. By gentle stirring, the mass is melted with very little heat, which causes the membrane to contract, and the albuminous portions to shrivel up, at the same time allowing the tallow to flow out. The mass is allowed to settle and is afterwards drawn off by a tap. Having been strained, it is mixed with from four to five parts of alum per thousand, which easily and completely separates the remaining impurities. After six to seven hours' standing, the clarified fat is racked off into conical wooden casks, where it is allowed to cool. The residue or refuse left in the copper vessel is scooped out and placed in a screw press, to extract more of the fat; and the pressed cake, consisting of the animal membrane, the fat tissues, muscle, blood corpuscles, particles of bone, and other impurities, together with 10 or 15 per cent. of unexpressed fat, is used under the name of greaves for manure and as dog-feed.

Treatment of Tallow with Acid.—Darcet has proposed the use of sulphuric acid to facilitate the extraction from the raw material. On the large scale a copper vessel, which can be heated with steam, and of about 1,200 litres capacity, is employed, 50 kilograms of the muddy acid liquors from a previous operation are added, together with four successive portions of 250 kilograms each of chopped fat, and 5 kilograms of sulphuric acid (1·846 sp. gr.) in 150 litres of water. The vessel is covered and heated for 2½ hours at 105° to 110° C. At this temperature the sulphuric acid acts on the skin, allowing the fat to melt out freely, and when this process is used an unimportant amount of fat is left in the refuse. The liquid fat is now run off and mixed with a solution of 1½ to 2 kilograms of alum in 20 litres of water. The mass is allowed to settle during 8 to 10 hours, and afterwards the fat, now floating in a clear condition on the surface, is placed in casks. By the acid treatment 83 to 85 per cent. of tallow is obtained, whilst by the ordinary method it is only possible to get 80 to 82 per cent. On the other hand, the last method yields, as above mentioned, a refuse having a market value of 12 to 15 francs per 100 kilograms. The tallow prepared with acid is in winter hard and white, but in summer a liquid fat settles out, whilst the other kind of tallow is more uniform. At this period of the year the candle makers prefer to use the tallow which has been purified without acid. It appears that the acid separates some of the olein from the stearin, and causes the formation of a certain amount of free fatty acid, which separates out by the slow cooling of the fat (a process necessary in the hot seasons of the year), and renders the product less homogeneous than otherwise.

The method adopted by Evrard at Douai is as follows:—

The crude fat, in the same condition as taken from the animal, without having been cut up or freed from flesh, etc., is treated with a dilute solution of caustic soda. The soda ley by penetrating the membrane, inflates and dissolves it, allowing the fat easily to flow from its skin envelope. In addition to fixing the offensive smelling fatty acids by their combination with the alkali, it has the advantage over any other method of producing after once washing with water a very white inodorous

fat; and as the temperature of 100° is never exceeded, there is no possibility of overheating. 800 kilograms of tallow can be melted per day by the following arrangement:—10 sheet-iron cylinders, each of 1 metre in diameter, and 1 metre 25 centimetres deep, and furnished, 17 centimetres above the ground, with a false bottom, having perforations of 3 millimetres each in diameter, are placed side by side. Steam can be conducted under the false bottom by means of a perforated steam pipe. Three hectolitres of soda ley, of specific gravity 1·25, are mixed in each vessel with 400 kilograms of fat and heated with a jet of steam; and that the fat may be quite immersed in the alkali, a second perforated plate is placed on the top of the mixture. This works upon vertical rods, in such a way that it falls of its own weight, or it may be pressed down by the hand. The fat rises above the perforated plate as soon as the alkaline solution has penetrated and dissolved the membrane. After about three hours' boiling the two plates almost touch each other, leaving but a modicum of fat with the skin refuse between the two plates. The steam is then turned off, and the soda liquor drawn off by a lower tap, and clean water having been run in for a short time, the vessel is again heated with steam. After the contents of the cylinder have been allowed to settle, the fat is run off from the aqueous solution into copper vessels 1 metre in length with a diameter of 75 centimetres, and two of these are required for each of the larger vessels. These twenty cylinders are heated in one large water bath. After standing twelve hours the tallow is siphoned into a copper cooler, and afterwards placed in casks to give it the commercial form; or it is at once worked up into candles. The alkaline and aqueous liquids are poured into sheet-iron vessels worked on the Florentine principle, in which the exit tube from the bottom of the first leads into the upper part of the second vessel, and so on throughout the series, and in this manner the fat collects on the surface, allowing the liquid underneath to flow out. The alkaline liquid that separates, still containing the odorous fatty acids which have been dissolved by the soda, is decomposed in wooden vats with dilute sulphuric acid, and the fatty acid rising to the surface is separated from the saline solution in the way just described.

The fatty mixture so obtained, consisting of offensive-smelling and coloured fatty acids with ½ to 1½ per cent. by weight of pure fat, is used in the manufacture of common soap.

Many plans have been suggested to prevent the offensive odours always arising in tallow melting. Amongst those plans in which the melting pots are provided with covers through which the gases are conducted into a flue or are previously burnt, the following is almost the only one which answers successfully. Fig. 442 represents

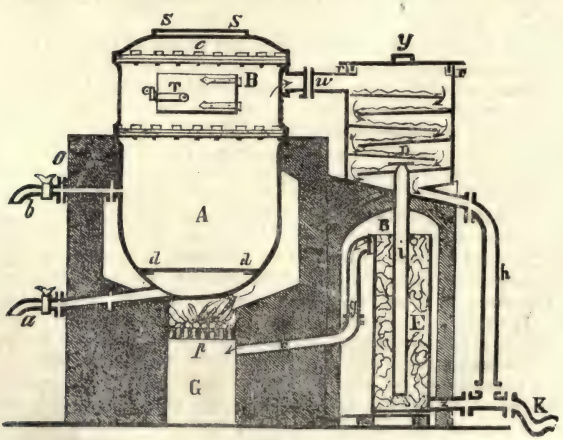


FIG. 442.

H. Vohl's covered apparatus for tallow melting. A is a cast-iron vessel, lined with sheet lead, with a riddled bottom *d d*; *a* is a tap to draw off the aqueous liquid; *b* is the tap through which the fat is drawn, *p* is the fire-grate. B is a cast-iron ring with door T for filling the pot, *c* the cover, with a mica plate S S. In the door T is also an aperture covered with mica for the purpose of seeing into the interior; D is the vessel into which the gases given off in the melting process are passed by the tube *w*; *y* is a cover with sand joints *r r*; powdered lime is placed in the

inside of D on oblique shelves to retain the offensive smelling products. The condensed liquid flows off through the pipe (*h*), and the gases and steam pass through into the condenser (E), which contains coke moistened with sulphuric acid. The liquid which is here condensed, passes through the pipes (Z and K), whilst the gas passes from *g* along the tube F into the ash pit (G) under the furnace. G is enclosed by an iron door, through which a powerful draught of air can be sent, carrying with it all the gas from the apparatus into the furnace. The waste gas from the furnace passes out at *o*. In the manufactory of Arlot and Co. at La Villette, the fat is melted in pear-shaped and perpendicular cauldrons placed directly over the fire. The manhole is closely fastened during the working, and the gases force their way through another opening to a channel which is common to 16 cauldrons. The mixed gases before reaching the large furnace are carried over the grate of a second or auxiliary furnace which is kept in a red-hot state by a separate fire, so that the gases may be completely consumed before passing into the chimney. It has not been found satisfactory to lead the vapours direct to the cauldron furnace, in consequence of the draught being so diminished as to be insufficient to support the heat necessary for the melting operation. A better combustion of the gases ensues if they are carried over the hottest part of the furnace.

Stein has proposed to absorb the noxious vapours and to render them innocuous, before allowing them to escape into the atmosphere, by a layer of wood charcoal and lime placed to the depth of 3 to 4 inches on a perforated plate over each cauldron.

In addition to the disadvantage arising from the necessity of using a fresh layer of deodorising material at every melting, the cauldron must be fitted with special contrivances (such as a false bottom, steam heat, etc.) made necessary by the stirring required during the melting operation.

The different kinds of fat and oil derived from plants are generally extracted by a simple mechanical operation of pressing the seeds and other parts of the plants which contain these substances in large proportion. Heat is sometimes applied to facilitate the extraction of the oil; but the product thus obtained is almost invariably inferior to that extracted without heat, or as it is termed cold drawn. Oil is extracted from the livers and other parts of fish in the same manner, as well as from various marine animals, such as the whale, seals, etc.

Of the Principal Kinds of Oil that are Liquid at the ordinary Temperature.—Olive oil is obtained by pressing the fruit of the olive tree (*Olea europœa*), a native of Asia, growing luxuriantly in the south of Europe. Oil of almonds is the fixed oil obtained by expression from the fruit of the almond tree (*Amygdalus communis*). Rape or colza oil is expressed from the seeds of various species of *Brasicca*, and nut oil from the fruit of the ground nut (*Arachis hypogœa*). Linseed oil is expressed from the seeds of the common flax (*Linum usitatissimum*), and cotton seed oil from the seeds of the cotton plant (*Gossypium barbadense*, and other species): these two oils have siccative properties. Train oil is obtained by boiling the blubber of various species of whales, especially *Balæna mysticetus*, but the sperm whale (*Physeta macrocephalus*) yields sperm oil. Cod liver oil is obtained principally from livers of the common cod (*Gadus Morrhua*), the best quality being extracted without heat and the commoner kinds by heat and pressure; seal oil is obtained similarly from the fat of different species of seals. Lard oil is the liquid oil that separates when pig's fat is subjected to pressure.

Of the Principal Solid Fats.—Palm oil is obtained by bruising and boiling with water the fruit of a palm (*Elais guianensis*) growing in Western Africa. Cocoa nut oil is obtained by pressing or boiling the kernel of the fruit of the cocoa nut palm (*Cocos nucifera*). Cacao butter is obtained by expression from the seeds of the *Theobroma Cacao*. Butter is the fat separated by churning from cow's milk. Lard is prepared by melting the fat of pigs, and separated from the membranes by straining.

Purification of Fish Oil.—For some time past Payen has recommended the purification of fish oil by warming it in deep copper vessels, placed in a water bath; and then in the same vessels, allowing the oil to cool very slowly to a temperature of 12° to 15°. A viscid but somewhat firm fat remains at the bottom, whilst the oil can be separated by decantation. The residue is mixed with others of a like nature in a copper vessel, where, after some time, a further decantation of oil is possible, and it can thus be very completely separated. The further clearing of both products is carried out in the following manner: the firm fat, about 5 to 10 per cent. of the whole, is melted in a wooden vat by allowing steam to enter freely. At the temperature of 100°, 1 to 2 per cent. of muriatic acid or tartaric acid is added. The mass having been well stirred is allowed to cool as slowly as possible, which is attained by wrapping a non-conducting material round the melting tub. The fat will now be found to be much

firmer and whiter, as a considerable quantity of the impurity has been either destroyed or retained by the acid. The liquid oil thus separated is heated to 100°, then violently stirred after mixing with it 1 per cent. by volume of a saturated solution of caustic potash (1·453 sp. gr.), which saponifies the noxious part of the oil, whilst the oil itself is left clear and colourless. As a final operation the oil is filtered through woollen bags. The soap residue is dissolved in water, and the fatty acids precipitated from their potash compounds. In the purification of the much darker oil obtained from some kinds of fish it is preferable to use 1 per cent. by volume of soda ley.

MANUFACTURE OF SOAP.

It has been already explained that when fatty acids or the neutral fats are heated with alkaline or other bases, combination or decomposition occurs, and that salts of the fatty acids are formed. The commercial production of these salts, or 'soaps,' as they are termed, constitutes an immense industry, the consumption of soap as a cleansing agent increasing with advance in civilisation. Chemically speaking, any salt of a fatty acid is a soap; industrially, the term soap signifies an alkaline salt of a fatty acid. On treatment with water, these salts liberate alkali, and it is the alkali thus liberated which, by its action upon fatty and other impurities, renders them soluble in water, and thus produces the cleansing effect. The liberation of free alkali from soaps by water is due to the fact of their being split up into free alkali, and a more acid combination than the original soap. Thus, when ordinary hard soap is used in washing, the water decomposes it, resolving it into soluble free soda and curds; these curds or insoluble flocks, which float on the surface of the water, consist of the sodium salt of a fatty acid; but it is a combination of an acid character, in which the fatty acid is not combined with soda to its fullest possible extent. It is not unlikely that in the future fatty acids will be replaced in the manufacture of soap by other cheaper acids—such as silica, a substance capable of forming soluble salts with alkaline bases, which is, indeed, already largely employed in the production of what is termed silicated soap.

Without repeating what has been described in another place (see p. 664) regarding saponification, it is sufficient here to point out that fats and fatty acids give rise to soaps when acted upon by alkalies, as represented by the two following equations:

$$C_{18}H_{36}O_2 + NaHO = C_{18}H_{35}NaO_2 + H_2O.$$

$$C_3H_5 3C_{18}H_{35}O_2 + 3NaHO = \left.\begin{matrix} C_3H_5 \\ H_3 \end{matrix}\right\} O_3 + 3C_{18}H_{35}NaO_2.$$

The latter equation serves to represent the manner in which all fats or glycerides decompose when saponified with basic oxides. Ordinary fats (including fixed oils) are constituted of glycerin—a triatomic alcohol—($C_3H_5 3HO$), in which three hydroxyls are substituted by the residues of fatty acids. Thus, in the instance represented above, tri-stearin or glyceryl tri-stearate is taken. Other combinations however are known, and, indeed, a few are actually used in soap making, which differ somewhat from ordinary neutral fats. This will be seen in a better way by writing the typical formulæ of glycerin and an ordinary fat side by side:—

Glycerine.

$$C_3H_5\left\{\begin{matrix} HO \\ HO \\ HO \end{matrix}\right.$$

Tri-stearine.

$$C_3H_5\left\{\begin{matrix} C_{18}H_{35}O_2 \\ C_{18}H_{35}O_2 \\ C_{18}H_{35}O_2 \end{matrix}\right.$$

It is possible to substitute one hydroxyl in glycerin by a radical, not of a fatty acid nature, for instance phosphoryl, which would yield glycerophosphoric acid:

$$C_3H_5\left\{\begin{matrix} HO \\ HO \\ HO(OPO)HO \text{ or } C_3H_9PO_6 \end{matrix}\right.$$

From this substance others of a more complex nature may be obtained, and many are known, being mainly of animal origin. Thus the two residual hydroxyls may be replaced by two molecules of the same fatty acid, or by two distinct acids; thus with palmitic and stearic acids, the following compound would result:

$$\begin{matrix} C_{18}H_{35}O_2 \\ C_3H_5C_{16}H_{31}O_2 \\ OH(OPO)OH \end{matrix}$$

Still greater variations may be effected, and still more complex bodies result. For instance, one of the subsidiary hydroxyls in the group, phosphoryl, may be substituted

by the residue of any amine, and, in fact, compounds are obtained from the brain and bile which have this constitution :—

$$C_3H_5\begin{cases}C_{18}H_{33}O_2\\C_{16}H_{32}O_2\\OH(OPO)C_5H_{13}NO\end{cases}$$

Many such substances have been described by Strecker, Thudichum, and Kingzett, and they are saponifiable by alkalies in the same kind of way as ordinary fats. Thus the body above represented has a total formula of $C_{42}H_{84}NPO_8$, and decomposes by boiling with alkaline bases into oleate, palmitate, and glycerophosphate of the base employed, and the nitrogenous compound $C_{15}H_{13}NO$.

The yelk of eggs, formerly used in soap making, being obtained from the print works where only the albumin is used, contains a compound similar to that just described, and, indeed, its soap-making qualities are divided between this substance and the neutral tri-olein also contained in it.

The different kinds of soap in common use are classified as hard, soft, and silicated.

Hard soap is made with soda, and its hardness depends in a great degree upon the amount of stearic and palmitic acids contained in the fat which is employed; the combination of these acids with bases being firmer in consistency than the corresponding oleates.

The kinds of fat usually employed in making hard soaps are tallow, palm oil, cocoa-nut oil, etc.; in southern countries, coarse olive oil is also employed. Ordinary resin is often used in addition to these fats. The use of resin in soap making, in the proportion of about one fourth of the tallow employed, modifies the hardness of the soap, and increases its solubility. The use of resin in making both hard and soft soaps may be at once explained; it consists of pinic, sylvic, and colophonic acids, or oxidised products of turpentine, considerable quantities of which are obtained in the distillation of crude turpentine, etc. The resin is first purified and freed from colour by distillation in steam, after which it may be used for making soap either alone or in mixture with fat. The acids of resin are strong enough to decompose sodic carbonate, and their combinations with fixed alkaline bases are soaps, in the sense that on treatment with water they liberate alkali.

The pans, or coppers as they are termed, used in soap making are of various sizes, the larger ones being about 15 feet in diameter and as many feet in depth, and constructed of wrought-iron plates rivetted together. Such coppers can turn out from 25 to 30 tons of soap in one operation. Heat may be applied in several ways; in some instances the contents of the coppers are heated by a steam pipe passing into them; in other cases a steam jacket is used, while yet other manufacturers heat their pans by fire. These pans are first charged by the fat or oil, and resin (if it be desired to use it), and then to the mass is added a weak caustic soda ley of 1·05 specific gravity, and the whole boiled and stirred; saponification gradually ensues, or if it does not take place properly, the evil is remedied by the further addition of soda ley. From time to time stronger leys are run in, but these never exceed a gravity of about 1·09. When the alkali is in excess, a further quantity of fat or oil is added, then more soda, then fat again, and so on, finally adjusting and completing the saponification in the pans by the time they are nearly filled. A precaution which is always observed is that finally there is no considerable excess of alkali present.

The soap thus produced has next to be separated in a solid form from its solution, and this is effected by the addition of common salt to the mixture; soaps being insoluble in a strong solution of salt. About 10 lbs of salt are used to every 100 lbs. of fatty material employed. The soap thus precipitated floats in the state of a granular mass or curd, from which the spent ley containing the glycerin is run off, and the soap itself is boiled again with fresh weak ley, until a 'close' state or homogeneous mixture is obtained. The details of further operations now depend upon the kind of soap it is desired to turn out, but these are of a simple kind and need not be entered into particularly. The soap curd is allowed to remain quiescent for some hours, or a period ranging up to two days: in this way the ley subsides and the soap may be ladled from the top and transferred to cast-iron frames, where by cooling it solidifies. The final operation consists in cutting up the soap into slabs or bars by means of wires.

Soft soap is made for the most part from whale, seal, and linseed oils, tallow and resin in this country; hemp, linseed, and poppy, and other drying oils, as well as rape and train oils, are also used on the Continent. The manufacture resembles in all important points that of hard soap, with the difference that potash ley is used instead of soda. The potash solution (of from 9° to 110° B., specific gravity from 1·06 to 1·08), is made from pearlashes and American potashes. The boiling of the oil or fatty material with the weaker ley is continued, until the mixture becomes of a streaky appearance, when the stronger alkali is added to effect clarification, and the boiling

continued with continual stirring. After a time the soap begins to 'talk,' as the soap makers term the noise of the bursting bubbles, and when this happens, the heating is discontinued, and the soap is ready to pack in casks on cooling.

Mottled soap is often produced by the addition to the nearly finished soap of crude soda liquor, containing in solution the double sulphide of iron and sodium. As it falls through the soap, the iron is precipitated as oxide in veins, thus giving rise to the appearance of marble. At times other reagents, such as prussian blue, are used with the same object. Mottling is merely a trade practice, and serves no useful purpose.

Hard soap differs in composition, and contains from 20 to 30 per cent. water, 70 to 60 per cent. of fatty acids, and 8 to 10 per cent. alkaline base; while soft soap contains from 40 to 50 per cent. water, with 50 to 40 per cent. fatty acid, and from 10 to 12 per cent. potash.

Toilet soap is produced by dissolving ordinary curd soap, and incorporating with it perfumes or particular substances, the addition of which determines the name and character of the soap to be produced.

Silicated soap is now produced on a large scale, in particular by Messrs. W. Gossage and Sons, and it represents the most recent advance in soap making.

Silicated soap is a mixture of ordinary soap and soluble glass or alkaline silicates, which latter substances are possessed of detergent power, from the fact that by treatment with water they liberate alkali. Silicated soap is cheaper than ordinary soap, and besides its domestic employment, it admits, therefore, of use in certain manufacturing processes—such as the fulling of woollen goods—when operations of cleansing are involved.

The soluble glass is first made by melting 9 parts of soda ash (of 50 per cent. caustic soda) with 11 parts of clean sand; while when soft soaps are required, equal weights of carbonate of potash and sand are taken. The melted glass is ground, then dissolved by boiling in water rendered alkaline, and the solution thus obtained is mixed with the ordinary soap by a mechanical stirring apparatus.

In 1852 Great Britain produced 83,200 tons, about one-half of which was made in Lancashire. In 1870 Lancashire alone produced as much as the whole of Great Britain had produced in 1852.

ARTIFICIAL LIGHT AND LIGHTING MATERIALS.

One of the most important applications of fat and oil is that of burning for the production of light. Towards the end of the eighteenth century animal fat, such as tallow and several kinds of oil obtained from fish, were the only materials used in this way, the former being used as candles, the latter for burning in lamps. Since that time other kinds of oil derived from plants have been introduced into use for this purpose, and considerable improvements have been made in the preparation of the material for candles. Combustible substances of mineral origin have also been brought into extensive use as light-producing materials. In burning any of these substances either in a lamp or in the form of a candle, they undergo decomposition of. such a nature as to produce combustible gas, and in both cases it is the combustion of this gas, as it is formed, that gives rise to the luminous flame. The special production of gas suitable for burning in this way, and capable of being stored up for use when required or transported to considerable distances, is another improvement in the art of artificial lighting, beside which all others sink into comparative insignificance. The material employed for this purpose is coal, and the process by which combustible gas is obtained from it is essentially the same as that taking place in the flame of a candle or a lamp, except that the gas produced is not immediately consumed as in these cases, but is first conveyed in pipes to the place where it is to be burnt.

The industrial operations connected with the preparation of materials for artificial lighting may therefore be treated of under three heads—viz., the treatment of natural oil and fat, so as to render them suitable for burning in lamps, and for the manufacture of candles; the extraction of liquid and solid materials from petroleum as well as the production of analogous materials from bituminous minerals by destructive distillation; and, lastly, the production of gas from coal.

Preparation of Oil or Fat for Burning.—The kinds of oil now chiefly used for burning in lamps are sperm oil and rape or colza oil, and the preparation they undergo for the purpose is intended only to separate admixtures of mucus and other substances, which would give rise to incrustation of the wick with carbon.

The treatment to which tallow and other kinds of solid fat are subjected, in order to prepare them for making candles, is intended chiefly to increase the consistency of the various materials and reduce their fusibility. These objects are, to some extent,

attained by pressing the fat, so as to separate the olein or liquid portion from the solid constituents, stearin and palmitin. But the most effectual method is to decompose the fats by saponification, and then, after removing the glycerin, to separate the fatty acids by pressure. By this means also a candle material is obtained which is not liable to become rancid like natural fat. The separation of the fatty acids can be carried out in several ways: e.g. 1. By saponifying the fat with lime and decomposing the lime salt with acid. 2. By the use of very little lime simultaneously with high-pressure steam. 3. By decomposition with sulphuric acid. 4. By means of superheated steam. Beef and mutton tallow, and latterly also palm oil, chiefly serve as the raw material for the preparation of stearic acid. Mutton tallow contains the most stearic acid, but the other fats, palm oil especially, are generally much cheaper, and these are now being more largely employed for this purpose.

Saponification with Lime.—The lime used must be as pure as possible. It is mixed with 10 times its weight of water, and then passed through a fine wire sieve. 1000 kilograms of tallow are mixed with 1,600 kilograms of water, in a wide wooden vat lined with sheet lead, of 4,000 litres capacity. This vessel is heated by means of steam so as to melt the fat, and milk of lime containing 140 kilograms of burnt lime is added. In order to facilitate the action of the lime the mixture must be kept stirred either by manual or by mechanical appliances. A hard insoluble lime soap is formed, and the water holdst he glycerin dissolved. The whole of the fat is saponified after 6 to 8 hours heating, and the aqueous solution is separated. In many manufactories, in order to save time, the still warm and consequently soft soap is mixed in the same vat with sulphuric acid. In other works, on the contrary, the cold soap is pulverised and sifted, then decomposed with sulphuric acid in a fresh vessel of the same form and capacity as the first. Ordinary chamber acid or concentrated acid of 1·846 sp. gr. will decompose the lime soap, although it is preferable to use acid of 1·21 sp. gr. 140 parts by weight of lime theoretically require 245 parts of sulphuric acid, but to ensure a successful operation it is usual to employ 274 parts of sulphuric acid for every 140 parts of lime used. About three hours are occupied to effect the decomposition, which results in the formation of stearic acid and sulphate of lime. At the termination of the operation the sulphate of lime is deposited at the bottom of the vat, whilst the fatty acids swim as an oily layer on the top of the acid liquid.

Washing the fatty acid.—The fatty acids are brought into a vessel of the same shape and arrangement as the one used in decomposing the soap, and then to remove the last traces of lime it is warmed with sulphuric acid of 1·091 sp. gr. As a final operation to remove the excess of acid it is once washed into water. The washing processes are conducted at a temperature of 100°. The yield of fatty acids of course varies with the kind and the purity of the fat employed. According to R. Wagner, tallow gives 94·4 per cent. of fatty acids, which contain about 46 per cent. of solid acid as stearic acid and palmitic acid.

Crystallisation.—The washed fatty acids are placed in moulds made of tin plate somewhat wide and of a capacity of 3½ litres each: here by cooling the mass solidifies to slightly coloured cakes, each of which weighs about 2 kilograms. To separate the impure and coloured oleic acid the solid cakes are pressed first cold and finally hot.

Cold pressure.—Each cake of fatty acids is wrapped in woollen cloths and placed under an ordinary hydraulic press in alternate layers of press bags and zinc plates, to the height of one metre, and in this way subjected to a gradual and increasing pressure for from 5 to 6 hours. By this means the greater part of the oleic acid is expressed, but by cold pressure it is impossible to get rid of the last portions; it has therefore to be subjected to hot pressure at about 40°.

Hot pressing.—The cakes to be pressed are wrapped in horse-hair cloths, and placed between hot iron plates in an hydraulic press arranged so that the whole can be heated by steam. The expressed oleic acid is run off into a reservoir where, by slow cooling, more solid acid separates and is recovered by cold pressing, and afterwards added to a large batch for hot pressing.

The solid cakes of fatty acids after hot pressure have once more to be refined in order to eliminate the last portions of lime. For this purpose they are melted with hot dilute sulphuric acid of 1·022 sp. gr., in a large vat: the mass washed with hot water, then clarified with albumin. In this way stearic acid is completely purified, and is ready for the market, either as cakes or in candles. To prevent the loss of sulphuric acid in the form of gypsum, it has been proposed to use baryta, or alumina in the form of sodic aluminate, instead of lime for the saponification; these would, by the after process with acid, become respectively sulphate of baryta and sulphates of soda and alumina. But neither method has been much used, partly on account of the heavy mass of baryta required, but also because lately in large manufactories quite a different process has been carried on.

Saponification with very little Lime, with the simultaneous employment of High-pressure Steam.—De Milly has found that the decomposition of the tallow can be completed by using 3 per cent. of lime instead of 14 per cent. by weight, but increasing the temperature in an enclosed vessel by means of high-pressure steam to 172°, which answers to eight atmospheres. The chief advantage presented by this process is of course in using less lime, thereby preventing expenditure of sulphuric acid. The reason of so little lime doing the work lies in the fact that high-pressure steam by itself, as fully described before (p. 664), splits up the fatty bodies into glycerin and fatty acids. The small quantity of lime serves a subordinate part, by preventing the re-formation of glycerides by the action of the free acids and glycerin on one another. The starting of the process is also due to the lime.

The apparatus devised by De Milly consists of a vertical vessel of strong copper or iron sheeting lined with lead, of two metres in height and one metre in diameter. The melted tallow is poured from a reservoir into the vessel through a narrow tube, and a second tube serves as an exit passage for the vapours. There is also a third pipe passing through the middle and reaching almost to the bottom, which serves for emptying the vessel; the cylinder is provided in addition with a man-hole at the side for the introduction of the lime, and with a thermometer, a manometer, and with a safety valve to resist a pressure of ten atmospheres.

2,300 parts by weight of tallow are placed in the melting pot and mixed with 2,000 parts of milk of lime (containing 69 parts of lime) having been previously made hot by steam. Steam under a pressure of 10 atmospheres is then allowed to enter by the steam cock, from the lower part of the vessel, and exerts a pressure of about 8 atmospheres, which is equivalent to a temperature of 172°. High-pressure steam corresponds to the following temperatures :—

5	atmospheres	152°
6	„	160°
7	„	166°
8	„	172°
9	„	177°
10	„	182°

The decomposition is accomplished in 7 hours; the steam cock is then closed and the temperature lowered to 130° for 30 to 40 minutes. The aqueous liquid containing the glycerin is drawn off, and can be used at the next operation instead of water. In this way the glycerin is incidentally concentrated. The mixture of the fatty acids and soap floating on the surface having been separated from the lower liquids is decomposed in a vat lined with lead, by means of sulphuric acid, in a manner similar to that explained above for the old process. As here, however, the chief part of the fatty body consists of free acid with only a small quantity of lime soap, just sufficient sulphuric acid and no more is used for the decomposition (namely 133 parts), nor is it necessary to pulverise the soap as it lies finely divided in the fatty acids. All the principal operations of washing, etc., to be carried out with the fatty acids are the same as in the old method.

Decomposition of the Fatty Bodies by Sulphuric Acid with subsequent Distillation.—According to the observations of Fremy, fatty bodies are split up by concentrated sulphuric acid into sulpho-glyceric acid and the sulpho-fatty acids. These compounds are decomposed by treatment with boiling water into free glycerine and sulphuric acid, which are dissolved, and into the insoluble fatty acids. On this reaction is based a new method of separation, which is specially adapted for impure fatty bodies such as kitchen refuse, butcher's offal, and the like, but more particularly for palm oil, as the fat acid separated in this way is afterwards subjected to distillation.

There is a great variation observed in factories working the methods of Gwyne, Wilson, and Coley Jones, in the strength of the sulphuric acid, in the temperature employed, and in the time occupied for the operation. Usually 12 to 16 per cent. by weight of concentrated sulphuric acid serves for tallow, 10 to 13 per cent. for fat refuse, and 8 to 9 per cent. for palm oil. The temperature is raised or the time of operating is lengthened as the proportion of sulphuric acid is lowered. Fatty refuse requires a special process of purification. Soap waste, from the washing of fleeces for wool spinning, is treated with sulphuric acid, and the floating fatty layer having been skimmed off by wooden spoons, is melted down on the water bath and clarified. The oil which here separates is decanted off, and the solid dirty sediment is placed in linen bags and pressed. If the soap waste is largely contaminated with extraneous substances, such as wool cuttings, earth, etc., it must first be cold pressed to remove the water, and afterwards hot pressed for the fat, which is then further operated with in the manner above described. In order to extract the last portion of fat in the

woolly material, it is (after the hot pressing in which the major part has been extracted) mixed with boiling water, and then again pressed.

The crude residues are re-melted with dilute sulphuric acid in large lead-lined vats heated by steam, whereby some of the impure organic substances are dissolved, and the soap residues become decomposed. The separation of the water from the crude fat is carried out in reservoirs fitted on the Florentine system.

Bogaert's method consists in decomposing the soap water with muriatic acid, then pressing the fatty mass and heating to the boiling point by means of steam; after cooling, nitric acid is added.

The decomposition of the fatty bodies by means of sulphuric acid is carried on in the boiler A (fig. 443), which is made of strong iron or copper plates lined with lead. The steam used to heat it is led from D into the jacket C, and the surplus steam along with the condensed water passes out through E. Over the vessel is fitted a cylindrical body (B), of sheet iron lined with lead, and provided with a cover F having two windows for observation and a manhole. GGG is a large pipe which discharges from the apparatus the exceedingly foul gases, consisting of sulphurous acid, acrolein, etc., together with suspended particles of fat, over the cast-iron basin I into the ash pit H. AL is a stirrer ending in a perforated disk and moved backwards and forwards by means of the eccentric J L.

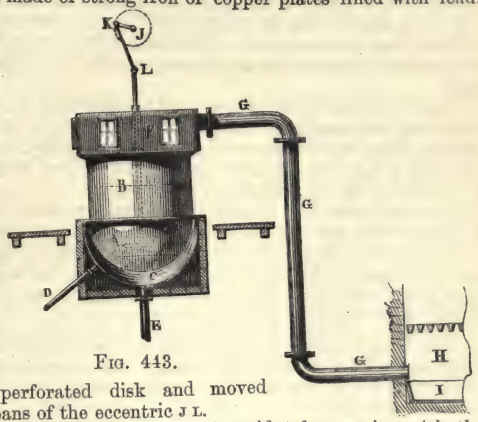


FIG. 443.

As already stated above, the quantity of sulphuric acid taken varies with the kind of fat that is to be refined. The temperature of the mixture is raised from 100° to 115°, and the operation is continued for twelve to eighteen hours. From time to time a sample is taken from the melting pot, and when this solidifies to a hard cake, and the violet colour which appears at the commencement of the operation has disappeared, the action is completed.

Washing the crude fatty acids.—When the decomposition is sufficiently advanced, the mass is allowed to cool for two or three hours, and while still liquid is drawn off by syphons into the large reservoir A, fig. 444, which is half filled with water. Through the pipe *a*, steam is conducted from the boiler by the connecting pipe G H. The temperature being raised to 100°, the decomposition of sulpho-glyceric acid and the sulpho-fatty acids into glycerin, sulphuric acid, and the fatty acids commences. The liquid then passes under the dividing wall into a second reservoir B, where the temperature is also kept at 100° by the steam coming in through *b*. The third reservoir C serves the same purpose, steam entering at *c*. From the last receiver the liquid flows under a third dividing wall into the canal D, and thence is led into two or three more similar receptacles.

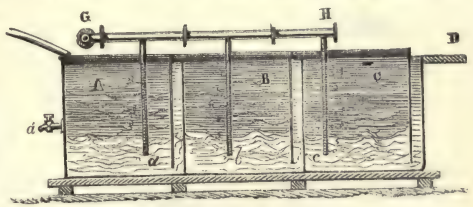


FIG. 444.

In this washing apparatus the fatty acids remain behind in the separators, while the specifically heavier watery liquid flows under the partitions.

The sulphuric acid treatment and the subsequent washing affect the melting points of the fatty bodies in the following manner:

	Melting points		
	In normal residue	After treatment with sulphuric acid	After washing at 100°
Bone fat . . .	24°	36°	33°
Palm oil . . .	30°	68°	44°

The washed fatty acids in the first reservoir A are drawn off above the water level through the cock *a'*, and are placed in the general receiver ready for the distilling apparatus. The fatty acids of the second and third receptacles B and C are poured back into the first and washed with a fresh portion. After every washing operation, there is taken from the bottom of the reservoir (A) a black deposit of a resinous consistency, amounting to about 4 to 10 per cent. of the original material. The application of this residue is described in detail afterwards.

Instead of sulphuric acid, latterly, chloride of zinc has been recommended for the decomposition of the fat, but it has not been approved of in practice.

The plan of Knab differs essentially from the one just described, inasmuch as the fat previously heated is mixed with hot acid, and the mixture after being allowed to act for a short time is poured into water. The decomposition thereby proceeds quicker, and in consequence of the short digestion with sulphuric acid much fewer products of decomposition are formed, and the yield of fatty acids is increased accordingly.

The fat is heated with concentrated sulphuric acid in a horizontal iron cylinder, and kept continually agitated. The mixture flows through the apparatus with sufficient rapidity to pass in about two minutes from one end to the other. It is then run into a vat which is three-quarter parts filled with boiling water, and the fatty acids floating on the surface can be separated.

The acid residue is so pure that there is no need to distil, but merely to melt it in the ordinary manner, and then subject it to cold and hot pressing. The quantity of acid used in Knab's process ranges in different manufactories from 4 to 15 per cent., the smaller the proportion of acid the higher must the temperature be raised. It is possible to obtain by this method about 90 to 95 per cent. of acids, whilst the older process will only yield 87 per cent.

Distillation.—As the fatty acids become contaminated during the sulphuric acid treatment with the black resinous substance before mentioned, they must be submitted to distillation; as the temperature required is very high, it is necessary to use high-pressure steam to prevent decomposition and an impure distillate. By the use of steam, the distillation will proceed between 170° and 230°, but in practice a higher temperature is generally used.

The fatty acids are placed in a vessel and heated by an arrangement of water bath in which the water flows back to the steam generator and keeps the temperature round the crude acids at about 45° to 50°. At this gentle heat the rest of the water and a few other impurities are separated by decantation. The liquid is afterwards heated in a square pan, D, fig. 445, having sides 6½ feet in length; over the

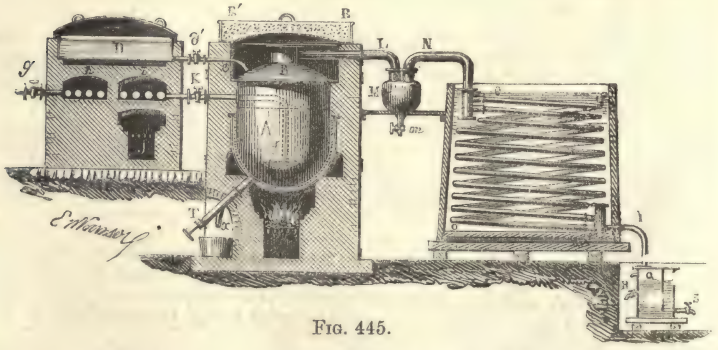


Fig. 445.

pan is a vaulted cover from which the condensed water trickles round and forms a luting to the cover. The heat is obtained from a fire which passes from the furnace J into the flues *h* and *i*, containing steam worms into which steam is introduced by the tube *g* from the steam boiler, and can be heated to 300°. In the distilling operation this steam is led by the cock K into the retort A.

The retort is of sheet-copper, about 3½ feet in diameter and 6 feet in height; the top B is rivetted on so as to be air-tight. The fatty acids are admitted through the tubes *e*, by opening the cocks *d'*. The retort is heated by means of a sand bath of cast iron placed at an interval of about an inch, and reaching up to about ⅔ of the height of the retort. On the cover B is the man-hole, and above all is the cover plate B' B' of sheet iron filled in with ashes to keep in the heat. As soon as the tempera-

ture of 250° is reached, known by means of thermometers placed in the retort, the steam cock K is opened, and steam led in at the temperature of about 250° to 300°. The steam tube ends in a circle *f*, from which the steam issuing from a great number of small holes is strongly forced into the liquid fatty acids. The temperature of the steam is observed from a thermometer placed near the steam cock K.

The steam carries over the fatty acids by the connecting tube L, through the middle vessel M, into the double worm O O. The receiver M serves to arrest the first distillate, which consists of impurities, and can be drawn off at once. The fatty acids flow into the worm O O, thence by the pipe P into the receiver Q, arranged on the Florentine system.

The lighter fatty acids swim on the surface of the water in the first division of the receiver, and the water forces itself under the partition into the second division. The fatty acids are drawn off at R and the water at S. The composition of the acids successively distilled depends on the time occupied in the distilling process as well as on the quality of the raw material.

The following table shows the melting points of the distillates:—

	Kitchen and Bone Fat	Palm Oil
1st product	40°	54·5°
2nd „	41°	52°
3rd „	41°	48°
4th „	42·5°	46°
5th „	44°	44°
6th „	45°	41°
7th „	41°	39·5°

The quantity of acids usually submitted to distillation in an apparatus of the size above described is about one ton, and the time occupied in distilling this quantity is about twelve to fifteen hours. The residue left in the retort is of a brown tarry nature, and is run off by opening the valve T, through the tube *x*, into a receiver, where, on cooling, it solidifies to an asphalte- or bituminous-like body, equal in amount to about 6 or 7 per cent. of the crude bone fat employed.

100 parts palm oil of the consistency of butter give 75 to 80 parts of distilled fatty acids—a yield equal to 50 to 52 parts of pressed acids.

Apparatus for Continuous Distillation.—An engraving of such an apparatus is shown in figs. 446 and 447. It consists of an horizontal cylinder B, which is heated by a lead bath G G. An ordinary man-hole permits access to the interior of the cylinder. The fatty acids, in a melted condition, flow in a thin continuous stream through the funnel C from a tap above it, the quantity being regulated by a float, in connection with the tap, shutting or opening it by its rise and fall, according to the level in the cylinder B. As soon as the fatty acids in the cylinder reach the temperature of 300° a stream of steam is sent in through D D. The mixture of acids and steam passes out through the discharge pipe (F) into the condenser. The intervening vessel E serves to retain the water condensing in the conduit tube from the ingressing steam.

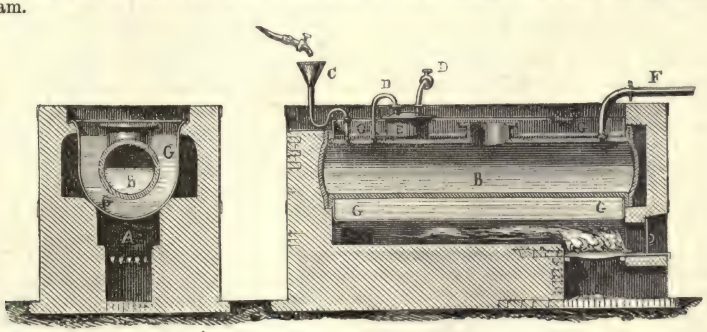


FIG. 446. FIG. 447.

Instead of employing steam at the normal temperature, which is barely 100°, latterly superheated steam at 250° has been used, and the steam pipe D has also been placed horizontally on the bottom of B and furnished with many small holes for the steam to pass upwards through the melted mass. After three to four days' working a residue will have collected in great quantity in B, and must be drawn off by an arrangement similar to that of T (fig. 445).

There has also been a still constructed in which the fatty acids are heated without the intervention of a bath, by means of hot air from the furnace used for the production of the steam necessary in the distillation. Masse and Tribouillet have introduced a still of this description into their manufactory at Neuilly.

Pressing and Purification.—The distilled products are separated according to their different degrees of purity. The first distillate with a melting point of between 54·5° and 56° can at once be used for candle making, but the after distillates, containing liquid and coloured acids, must be first cold pressed and then hot pressed.

The pressed cakes are melted in large tubs with water, which has had the lime previously precipitated with oxalic acid.

The following table gives the quantity obtainable from the raw material by the sulphuric acid treatment:—

Soap suds obtained by wool washing from Rheims	50–55 per cent.
„ „ „ from Tourcoing	47–50 „
Thick olive oil	55–60 „
Palm oil	75–80 „
Fat from slaughter houses	60–66 „
Oleic acid from stearin works	25–30 „

Decomposition of Fat by Superheated Steam.—After Tilghmann had found that fatty bodies could be decomposed by superheated steam, various pieces of apparatus were devised wherein this action was technically employed. Tilghmann subjects a mixture of the fatty body and water, circulating in a system of tubes, to a heat of from 330° to 350°. The decomposed liquid is then passed through a spiral cooler, where it is cooled to 100°; thence it passes to a receiver in which the two layers—aqueous and fatty—can be separated.

Wilson and Gwyne heat the fatty bodies in retorts to 290° to 315° and then pass, for twenty-four to thirty hours, steam heated to 315°. The escaping vapours are condensed in a worm. This method is used in England and in Russia.

One hundred pounds of tallow should give sixty-six pounds of stearic acid, against 45 to 50 per cent. by the older process.

Manufacture of Candles.—The operations merely consist in melting and shaping the material of which the candles are to be made, and at the same time inserting a cotton wick in the centre of the candle. Besides tallow and the fats prepared in the manner already described, several other materials are used for making candles, such as wax, spermaceti, paraffin, etc.

Dipped Candles.—15 to 20 wicks suspended from a thin stick of light wood are dipped all together into tallow which is just at the point of solidification. The wicks with adhering tallow are brought out and cooled and the operation of redipping and cooling is successively performed until each candle is considered to be of sufficient thickness and of the required weight. Dipped candles are conical in shape, and are thinner at the top than at the bottom. They are cheap and in some places still preferred.

Moulded Candles.—A very gentle heat is sufficient to melt the tallow which is used for this purpose. The moulds are prepared, slightly conical in form, from an alloy of one part tin and two parts lead. Through each mould passes a wick of twisted cotton thread, which, in order to keep it in position, is fastened to a cross bar above and below to a plug, which at the same time serves as a stopper to the aperture. The moulds are suspended in great numbers from a frame, and the tallow, in not too hot a condition, is run in through a funnel at the top. The tallow having cooled, the candle is removed from the mould and the funnel-shaped head is cut off. The candles are now ready to be packed, and in such a way that from 6 to 12 equal a pound. The weight of cotton used is in the proportion of 1 part of cotton to 100 parts of tallow.

Stearin Candles.—The wicks used in these candles are generally made of twisted or plaited cotton threads, but sometimes, though seldom, of flax or hemp. The twisted wick is merely a screw-like thread, but in the plaited wick the separate threads twine through each other. Cambacères devised a method in which the wick was thin and so strongly plaited, that the tip of the wick turned to the outside of the flame and was consumed as the candle burnt down, so that it was not necessary to cut off the wick from time to time, as is required with the old twisted wicks, to prevent the obscuration of the flame by the deposition of soot. That the wicks may burn quickly and completely, they are dipped in an oxidising material such as saltpetre, chlorate of potash, etc.; also to prevent the inflation of the carbonised wicks, they are treated with such substances as boric acid, borax, sal ammoniac, phosphate and borate of ammonia, which melt with the ashes and fall aside from time to time.

It is essential that the thickness of the wick should be in the right proportion to the thickness of the candle. If it be too thin, a higher rim of unmelted tallow is formed round the candle: if it be too thick, no rim is formed at all, but the tallow continually gutters.

For candle making the stearic acid is melted on the water bath, and mixed with 1 to 5 per cent. of wax, or with paraffin in quantities up to 20 per cent. The further addition of such poisonous compounds as arsenious acid—a plan formerly adopted—has now been abandoned. The object of adding wax and paraffin is to destroy the crystalline structure of the stearic acid, and thus to render the candles less brittle and capable of burning more evenly. The stearic acid before being cast into the moulds is brought into a semi-solid condition which prevents in some degree a crystalline solidification of the mass.

The moulds (fig. 449) with the exception of having a larger funnel are similar to those used for tallow candles; a new form of mould recently in use has one funnel for thirty candles (figs. 450 and 451). In the upper part of each mould is a small disk, *a a'* (fig. 448), with a centre hole through which the wick is drawn and fastened there by being tied in a knot; at the bottom the wick is kept in its place by a small peg; instead of using the perforated plate at the top, the wick is sometimes fastened to a small holdfast. In order to obtain well-made candles, it is essential that the wicks should be held accurately in the axes of the moulds while they are being filled with the melted fat, so that after its solidification the wicks of the candles are in the centre throughout the whole length.

Fig. 448.



Fig. 449.

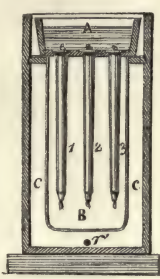


Fig. 450.

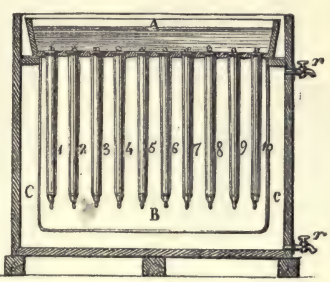


Fig. 451.

Before fixing the wicks, it is necessary to steep them in the solutions which shall serve the object of causing a steady combustion; and of the substances previously mentioned as serving this purpose, it is the custom to use boric acid.

The moulds with the wicks fastened in them are placed in a cast-iron vessel which can be so arranged as to be heated to 100° with water or with steam from the outside. To this end a great number of such vessels are placed air tight in a large wooden vat in which steam can play round the cast-iron vessel (*c c*, figs. 450 and 451). The fatty acids are run in as soon as the air bath is at 45°. The tap *r* allows the air to escape, and *r'* the condensation water.

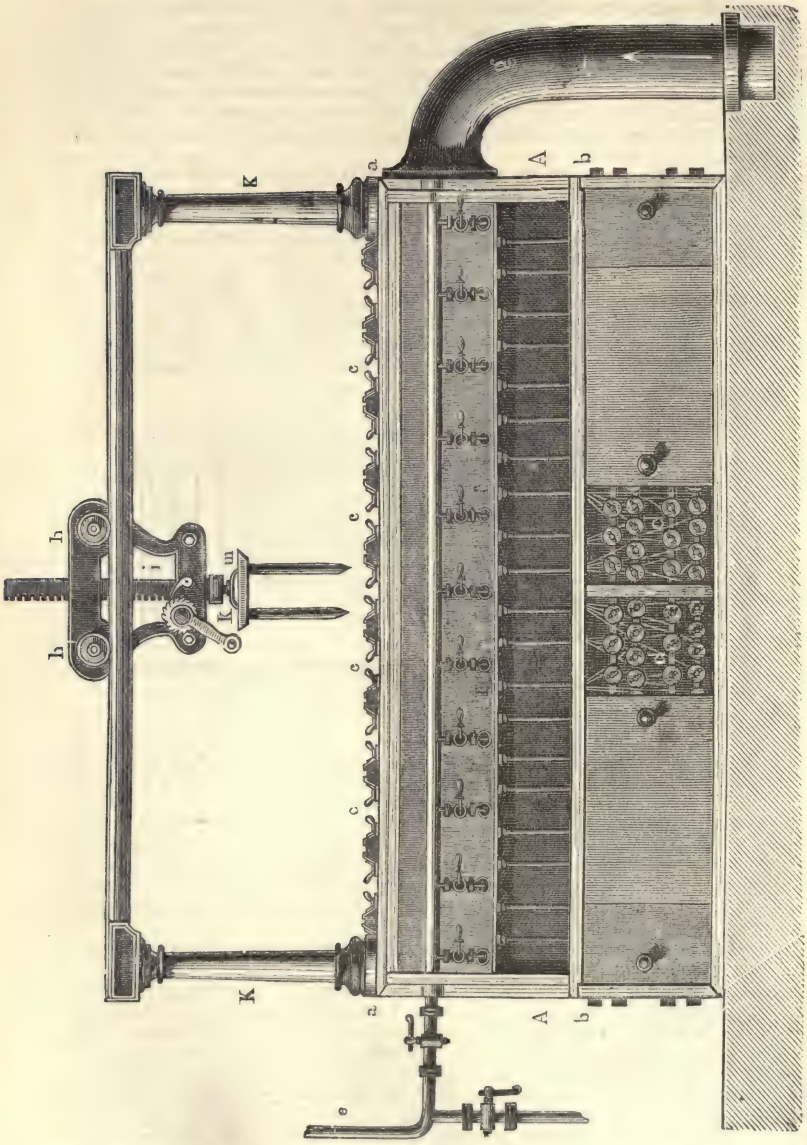
Instead of using steam in this way, the moulds may be heated in a water bath or in an air bath heated by hot pipes.

After being cooled the pegs are taken from the bottom of the moulds, and the wicks cut off underneath the disk *a a*. The waste cuttings, etc., are melted with tartaric acid either in a silver-plated or in a porcelain vessel and utilised at the next moulding. Should the candles adhere to the moulds, hot water must be applied externally.

The very short thick candles called night lights are made by running melted fat into metal moulds, or into paper cases of the requisite size, and, after the fat has solidified, the wicks, previously soaked in wax, are passed through the centre.

Moulding machines are now generally in use in stearin candle factories. One of this kind, the machine of Cahouet and Morgane, is shown in fig. 452. A A is the mould frame for 200 candles, having one filling funnel for every 20 moulds. The separate moulds are fixed between the plates *a a* and *b b*. At the bottom of the machine are reels for unwinding wicks, which are fastened above the plate *a a* by means of two rails pressed together, and capable of being drawn upwards by the lever arrangement *h h* on the stand K, which can be set in operation by the rack and pinion *i*. In the filling operation, the wicks are held and stretched above the moulds by the iron rails. By opening the cocks *f f*, steam passes from the main pipe *e* into

the moulds. The steam is first passed in to warm the moulds, then, after turning it off, the stearic acid is run into the moulds. Cold air is passed through from the ventilator *g* in order more quickly to cool the moulds. After complete solidifica-



tion, the wicks are drawn up by means of the above-mentioned apparatus *h h*, and with them the candles from the moulds; while simultaneously the necessary wicks for the next casting are drawn through. There only remains the final operation of cutting off the wicks above the rails and the tops of the candles.

Of the many other machines for this purpose it will suffice here to mention the American moulding machine of Francis Saase. The essential parts are the same as in the machine previously described, except that the finished candle is not removed

from the mould by the wick, but is pushed out by a peculiar contrivance, worked from below, consisting of a short metal barrel that also serves to conduct the wick from the reel to the mould, and having on the upper end a tin cone which exactly fits the mould and forms the bottom. After the solidification of the stearic acid the metal pipe is pushed upwards by a mechanical movement carrying with it the moulded candle now ready for removal. With the machine of Cahouet and Morgane, two persons are required, and can turn out 600 candles per hour, whilst one man can work four machines of Saase's and mould 1,200 candles per hour.

The candles are sometimes bleached by exposure to air and light, but this is an operation not always carried out.

Fig. 453 represents a machine for cutting and polishing. The candles having been placed in parallel layers in the box A, fall one after another into the gutter of the cylinder B, immediately under the circular saw C, which cuts off the ends: they then fall upon the woollen cloth drawn over the rollers G G G G and H H. The three large cylinders D D′ D″, also covered with woollen cloths, revolve in an opposite direction to G, at the same time moving quickly backwards and forwards in the direction of

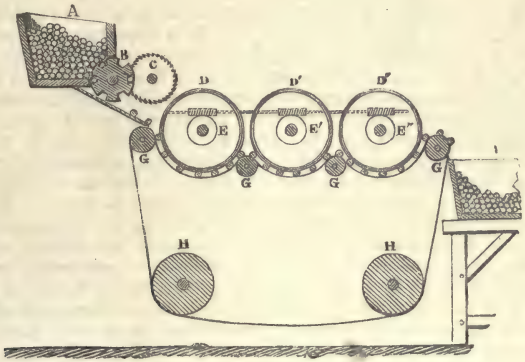


Fig. 453.

their longitudinal axes. In this way the candles passing between two friction cloths and being rubbed lengthways by the roller G, now fall quite polished and ready for packing into the box I.

The Various Kinds of Candles. Coloured Candles.—The dyeing material is placed in the melted fatty body before the moulding process. According to Vohl, the following compounds are the pigments used. For red, cinnabar, minium, dragon's blood, and alkanet root; for rose colour, madder lake and madder; for yellow, chromate of lead, sulphide of arsenic, chromate of zinc and turmeric; for green, Schweinfurt green, stearate of copper, verdigris, and a mixture of Berlin blue and chrome yellow; for blue, ultramarine. Amongst those named are some poisonous compounds, such as cinnabar, sulphide of arsenic, Schweinfurt green, and the use of them should be avoided.

The names 'Star,' 'Milly' and 'Apollo,' applied to stearin candles, have been derived from the Barrière d'Etoile, Paris, where De Milly started the first stearin candle works, and from the 'Apollo Company,' Vienna.

Palm candles are made of the fat acids prepared from palm oil.

The English composite candle is made from a mixture of stearic acid and cocoa-nut stearin; it has the lowest melting point of any kind of stearin candle.

Plated Tallow Candles.—These are not moulded but dipped, as in the ordinary dipping process, successively in three mixtures wherein the proportion of tallow decreases as the stearic acid increases, by which means a core of easily melting material is coated by a less fusible substance. Composition of the three mixtures:—

	1	2	3
Stearic acid	50	70	90
Tallow	44	24	5
Dammara resin	1	1	—
White resin	2	—	—
White wax	—	2	2
Camphor	3	3	3

Another method consists in filling moulds with stearic acid and allowing it to remain there sufficiently long to form a hard coating; then the unsolidified portion is turned out and its place filled with melted tallow.

Treatment of the Undistilled Residues.—The brown tarry retort residues obtained in the distillation after the sulphuric acid treatment can be used for the manufacture of illuminating gas; for this purpose, according to Payen, it is mixed with sawdust impregnated with the residue from the purification of rape oil. The residue without doubt could be used in the manufacture of common soap or as a japan for leather. If the dried residue be mixed with sawdust, and then extracted with carbon bisulphide, an appreciable quantity of fatty acids is obtained after distilling off the carbon bisulphide at 48° or 50°; the fatty acids can be then easily distilled by superheated steam.

The liquid oil obtained by cold pressure from crude fatty acids consists essentially of oleic acid, and can be used, partly as burning oil, partly for soap making. It is worthy of remark that for these purposes the oil obtained by the lime process is preferable to that which is prepared by the decomposition of the fatty body with sulphuric acid.

Estimation of Paraffin in Stearin Candles.—As it is now the custom to a very large extent to mix paraffin with stearic acid, it is important to have the means of qualitatively and quantitatively estimating both. R. Wagner has a qualitative method, in which the mixed bodies are dissolved in alcohol, heated to boiling, and mixed with an alcoholic solution of neutral acetate of lead. The presence of stearic acid is indicated by a flocculent precipitate, whilst pure paraffin gives no precipitate. Unfortunately, as a practical method, this is of but little use, as it is much more requisite to detect the presence of paraffin in stearin than of stearin in paraffin.

Hock gives the following method (Wagner's *Jahresber.* 1871, p. 858) for the qualitative and quantitative determination of paraffin in stearin. 5 grams of the mixture are saponified by potash ley of tolerable strength; the soap and the paraffin are precipitated by a concentrated solution of common salt, filtered, and the residue washed with cold water or with very dilute alcohol. The common salt and the soap are in solution whilst the paraffin remains behind on the filter. It is dried at 30° to 40°, and then dissolved in ether, filtered, and the ether evaporated in a porcelain capsule. The weight of the residue expresses the quantity of paraffin in 5 grams of the substance; the amount of stearic acid is obtained by difference.

Wax Candles.—The kinds of wax occurring in commerce are of various origin and differ in their composition as well as in their physical and chemical properties. The most important are the following:—

Bees' Wax.—This is formed in the plant from which it is collected by the bees and stored in the honeycomb. From the comb the wax is separated by a simple melting operation. Native wax, especially that produced by young bees, is of a light yellow colour, but the foreign sort is of a darker hue. It is brittle and granular; it begins to soften at 30° and melts at 62° to 63°. In ether, carbon bisulphide, benzol, fatty oils and in fats it is easily soluble; alcohol dissolves only a part, viz., cerotic acid, $\left.\begin{matrix}C_{27}H_{53}O\\H\end{matrix}\right\}O$, formerly called cerin, with some palmitic acid; the insoluble part consists essentially of myricylic palmitate, $\left.\begin{matrix}C_{16}H_{31}O\\C_{30}H_{61}\end{matrix}\right\}O$. There is a third constituent existing to a small extent, but of a composition still less understood. The varying quantity of the different constituents in wax of course affects the melting point. The best European bees' wax comes from Turkey and the Danube (Moldavia, Wallachia, Hungary, etc.) North Germany produces very good wax, but that from South Germany, Spain, and from France is very little valued. America, Asia Minor, Egypt, Morocco, and Barbary also supply very good wax.

Chinese Wax, or, Pe La wax, is collected by the wax insect (*Coccus ceriferus*), and deposited upon certain trees (*Rhus succedanea*). It is white in colour, hard and crystalline in fracture, and melts at 82°; it is soluble in ether. It essentially consists of cerotylic cerotate, $\left.\begin{matrix}C_{27}H_{53}O\\C_{27}H_{55}\end{matrix}\right\}O$.

Japanese Wax (also called American) occurs in round disks; it is white and brittle, soluble in boiling alcohol, and melts at 42°. It is probably a glyceride (glycerilic palmitate?) Another kind of vegetable wax is obtained from the rind of the fruit kernels of various trees, called by the Japanese lacquer trees. Sometimes the rind is removed from the kernels and steamed and pressed separately; sometimes the whole kernel is so treated. The wax separates as a bluish-green mass, which is purified by boiling it with alkali and then pouring it into cold water, when the wax separates from the impurities and floats on the top of the water. It is then bleached

by exposure to the sun, and the resulting white powder is melted to form a homogeneous mass.

Carnauba and Ocuba Wax both come from Brazil. The first forms a coating on the leaves of a kind of palm (*Corypha cerifera*). In consequence of its high melting point (83·5°) it is used to raise the fusibility of a low-melting wax.

Ocuba wax occurs in the nut of a shrub growing on the banks of the Amazon in the province of Para ; it is green in colour and melts at 36° to 48°.

Myrtle Wax is extracted by boiling, from the berry of *Myrica cerifera* occurring in the Southern States of North America. Its melting point is 46°.

Palm Wax is scraped from the bark of a palm (*Ceroxylon andicola*) found growing on the Cordilleras. It melts at 83° to 86°.

Andaquies Wax somewhat resembles bees' wax ; it is produced by an insect met with on the banks of the rivers Orinoco, Amazon and Magdalene. Its melting point is about 77°, and it therefore offers a very good candle-making material.

Wax Refining.—The object to attain is the separation of mechanical impurities. For this purpose the wax is melted in hot water, to which is added ¼ per cent. of alum or tartar, and occasionally sulphuric acid. The mixture is allowed to settle, when the impurities fall to the bottom and the wax floats on the surface ; after cooling it may either be remelted or at once bleached.

Wax Bleaching.—The primitive method of sun-bleaching is still in use by preference over any artificial process.

In order that a large surface may be exposed to the sun, it is usual to roll the wax in thin sheets, and for this purpose the melted wax is poured through a vessel having fine slits in the bottom on to a moistened roller on which it immediately solidifies in the form of bands, and thence falls into a vessel of water placed underneath. In this form the wax is exposed on linen sheets to the sun, and once daily sprinkled with water. As only the surface exposed to the sun is bleached, it is necessary to re-melt the wax, and go once or twice through the operation. In 20 to 40 days, according to the weather, the bleaching is completed. The wax is then melted, passed through a hair sieve, and cast into the required form. The loss in refining and bleaching by the process described varies from 2 to 10 per cent.

Many ways have been suggested for artificial bleaching, but as yet they have not been able to supersede the old method. Chlorine, bleaching powder, etc. cannot be employed, as they all tend to the decomposition of the wax. The best method, however, is by means of hydrogen peroxide, which is developed by melting the wax with oil of turpentine, rolling as before, and then exposing to the air. Other processes, such as the use of sulphuric acid and bichromate of potash or permanganate of potash, give but unsatisfactory results.

Wax Candles can be prepared by (1) pouring the wax on the wicks, (2) by drawing the wicks through the wax, (3) by moulding, (4) by pressing the wax through a mould.

The Pouring-on Process.—The wicks are suspended by hooks from a revolving ring, and the melted wax is poured on by a ladle from the top and allowed to solidify on the wicks. To ensure the uniform thickness of the candles the wicks are turned and the pouring on commenced again, until the candle is sufficiently thick. Frequently to save time and labour the wax is poured on at one operation, but great skill is necessary to do this. That the wicks may remain free at the 'burning-end,' they are fixed in small tin-plate caps. The still warm candle is now rolled until smooth between woollen cloths on a marble slab table by means of smooth boards. Having been so polished they are then bleached by exposure to air and light.

The drawing process is used for the most part for wax tapers and festival candles, and for these purposes the wax is almost always mixed with resin and turpentine, or with tallow. The wick is wound from a roller through melted wax contained in a heated copper vessel, thence through the hole of a horse-shoe-shaped drawing-plate, containing larger holes, on to another cylinder placed on the opposite side to the first. From the drawing-plate it again passes through the wax bath, and a larger hole of the horse-shoe on the first cylinder, and so on until the end of the operation.

The moulding of wax candles, an operation similar to that described for tallow and stearine candles (p. 677) is accompanied by the disadvantage of the wax shrinking ; in consequence, hollow places are liable to form near the wick, and the wax clings to the mould. This can be prevented to some extent by first dipping the wicks in wax and also by using glass moulds.

The method of enwrapping the wick with bands of wax is still generally employed for the manufacture of large candles. Soft wax is made in long strips on which the wick is placed lengthways ; the wick, having been covered with wax, the mass is then rolled on the marble-topped table until it has acquired the cylindrical

form. Another method is to take the cylinder of wax and to make a hole through the middle, then pass the wick through and fill in with melted wax.

Wax Candle Pressing.—The machine devised by Riess for this purpose is shown in fig. 454. It consists of a jacketed chamber (H), with a bent tube (T) for carrying the wicks; L, the tube for passing steam to the jacket (J) of the press cylinder; M is the pipe for efflux of condensation water; J, is the mould. The kneaded wax is poured from the side into the press chamber H, where it is made hot by the surrounding steam and pressed by means of a piston through the conical end of the pressing chamber. Simultaneously with the wax the wick is drawn through T into the mould (J,), and enveloped by the wax from T by a concentric; the strongly pressed candle roll is then passed over a roller, through cold water, to cool it. Other sized mouthpieces can be screwed on at T in order to vary the make of candles. This apparatus is specially adapted for the manufacture of wax tapers, and surpasses the older process above described, by the production of four to six times as many during the same time. The colouring materials used for wax are the same as for stearin.

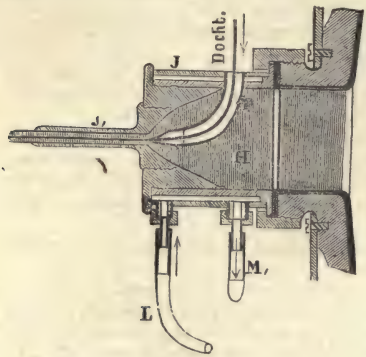


FIG. 454.

Wax is frequently adulterated with cheap materials, as rosin, paraffin, tallow, stearic acid, Japanese wax, etc. For the detection of paraffin, Landolt has proposed a plan based on the decomposition of wax by fuming sulphuric acid, and on the paraffin being unaltered by this treatment; the plan is only a qualitative test for the detection of a large quantity of paraffin.

Donath recommends the following method for the detection of impurities in wax. A piece of the wax, about the size of a nut, is boiled for five minutes with a concentrated solution of carbonate of soda. Thereupon one of two things may occur: either (A) an emulsion is formed remaining when cooled, and giving evidence of the presence of rosin, tallow, stearic acid, or Japanese wax; or (B) the wax swims completely as a fatty layer on the surface of the liquid, which is only somewhat yellow in colour, showing the wax to be pure or adulterated only with paraffin.

To determine the point (A) the suspected wax is boiled for a minute or so, with moderately strong potash ley, afterwards adding common salt. If a complete flocculent separation of soap (*a*) is produced, it is shown that all the substances under (A) excepting Japanese wax may be present; (*b*) a fine granular magma shows the presence of Japanese wax. (B) the detection of paraffin is best determined according to R. Wagner, by taking the specific gravity of the wax. If it be so low as 0·96, it can be assumed, in conjunction with the evidence given by the carbonate of soda treatment, that paraffin is present, and in such a case an estimate of the quantity of paraffin can be formed. On this principle R. Wagner has tabulated results of such admixtures deduced from the specific gravity.

Spermaceti Candles.—Spermaceti occurs in the bone cavities in the head of the whale, under its skin from the head to the tail, and in the flesh and blubber. It remains dissolved in the oil by the natural heat of the whale, but separates out when life is extinct. The crude solid spermaceti is purified by pressing away the oil and treating the residue with soda or potash ley, which saponifies any remaining oil. It is then washed with water, and the now purified spermaceti solidifies on cooling. About five tons of oil are obtained from one whale, and this yields 30 to 40 cwt. of solid spermaceti.

Pure spermaceti is white and crystallises in laminæ, having a mother-of-pearl appearance with a fatty feel. It melts at 48° and distils almost unchanged at 360°; it is soluble in alcohol. In its chemical composition it is cetylic palmitate, having the formula $\left.\begin{matrix} C_{16}H_{31}O \\ C_{16}H_{33} \end{matrix}\right\}O$, but it also contains a small quantity of another fat acid ether, with more carbon atoms.

Moulding Spermaceti Candles.—The operation is somewhat similar to that followed with stearine candles, except in this case it is necessary to afterwards run in spermaceti in the cavities round the wick, in consequence of the great contraction of spermaceti. The candles are taken from the moulds and polished by hand friction. It is customary to mix about 3 per cent. of wax or stearic acid with the spermaceti, to

destroy its crystalline texture. Spermaceti candles are very dear, but surpass all others by their alabaster appearance. They are used in large quantities, especially in England, by the wealthy classes.

Paraffin Candles.—The material known in commerce by the name of **paraffin**, and used for making candles on account of its similarity to wax and spermaceti in physical characters, consists of carbon and hydrogen combined in nearly the same proportions as in olefiant gas; but it is probably a mixture of several distinct hydrocarbons belonging to the marsh gas series, differing from the liquid and gaseous members of that series only in state of aggregation, and in the number of atomic proportions of carbon and hydrogen in the molecules, after the manner of homologous substances generally. The term 'paraffin' is therefore now employed by chemists as a generic designation of all the substances belonging to the marsh gas series, and it is only in regard to the technical application of those which are solid within the ordinary range of temperature, as candle material, that the name has a limited significance; in the same manner, since some of the liquid paraffins are used for burning in lamps, or for lubricating machinery, etc., they are also called **paraffin oil**.

Solid paraffins occur naturally as the minerals **ozokerite** or **earth wax**, and associated with liquid paraffins, as constituents of the various kinds of **petroleum**, and probably also as constituents of the volatile oils obtained from some plants. These substances also exist among the products obtained by the action of heat upon substances of organic origin, such as wood, and consequently they are present together with liquid paraffins, etc., in the tar resulting from the destructive distillation of peat, coal, bituminous shale, etc. The crude solid paraffin obtained from any of these sources often varies considerably in hardness and fusibility; and for making candles it requires to have the softer and more fusible portions separated. Its preparation forms a part of the hydrocarbon oil manufacture described below.

Candle paraffin is a colourless or bluish-white translucent substance, destitute of smell or taste; when warmed it softens and then melts, at temperatures ranging from 30° to 60° according to the source from which it has been obtained and the extent to which the more fusible portions have been separated. The specific gravity varies from ·870 to ·912. Paraffin is insoluble in water, and but sparingly soluble in cold alcohol, but it is copiously soluble in ether, turpentine, carbon disulphide, and hot alcohol. At ordinary temperatures it is not acted upon by concentrated acids or alkalies; it boils at a temperature above 300°, and is partially decomposed when distilled.

Hydrocarbon Oils; Paraffin, etc.—Materials of this kind, obtained either by the rectification of natural petroleum, or by the destructive distillation of wood, peat, or bituminous minerals, are now largely used as substitutes for candles, and for the different kinds of fat oils which were formerly the only source of artificial light.

The first impulse was given to this industry by Reichenbach, who, in 1830, prepared from beechwood tar both solid paraffin and an oil that could be burnt in suitably constructed lamps. But, owing to the small amounts in which these products were obtainable from tar or from the bituminous minerals then known, the various attempts made to bring them into practical application proved unsuccessful, until materials capable of yielding a larger amount of oily products were discovered. Among these the principal were a remarkable bituminous mineral, occurring in the coal measures at Boghead, in Scotland, and the tertiary coal or lignite occurring in several parts of Germany.

Not long after the industrial production of these hydrocarbon oils, etc., from bituminous minerals had become established, a further source of supply was furnished by the discovery of the vast deposits of petroleum in America, and at the present time, the liquid hydrocarbons analogous to paraffin, and associated with it in petroleum, as well as in the products of distillation, are very largely used for burning in lamps.

Petroleum or mineral oil occurs in many parts of the earth as a dark-coloured inflammable liquid, possessing a bituminous smell and various degrees of density, from 0·7 to 1·1. Some kinds that are thin and but slightly coloured, are known by the name of **naphtha**, while other kinds that are viscid and almost black are termed mineral tar. These different kinds of mineral oil occur chiefly in North America, Persia, the Caucasus, Georgia, Burmah, the Carpathians, Italy, some parts of Germany, and Switzerland, as well as in France and England to some extent.

The petroleum of Pennsylvania is a dark brownish-coloured mobile liquid having a specific gravity varying from ·782 to ·820, and a peculiar greenish fluorescence. Some of the petroleum occurring in America has a greater density; for instance, that known as Mecca oil, which is a thick viscid liquid having a specific gravity of from ·860 to ·910, and some of the Californian petroleum has a specific gravity of ·927. The petroleum of Canada has a very offensive odour, owing to the presence of sulphuretted compounds which render its purification difficult.

In America petroleum is obtained by boring deep wells, constructed in the same

manner as artesian wells, until a deposit of petroleum is tapped, and then it either rises to the surface and flows out in intermittent gushes, constituting what is termed a flowing well, or the petroleum has to be raised to the surface by means of a pump. The quantity obtained from these wells is sometimes very large. One of the great flowing wells at Enniskillen yielded as much as 600,000 gallons when first opened, but it was soon exhausted, and the greater number of wells yield only from 400 to 800 gallons daily, though some few have yielded as much as 4000 gallons a day.

In Wallachia petroleum is obtained from strata about thirty feet below the surface, and the wells are made by sinking square shafts lined with timber like rude water wells, and fitted with a windlass above, by means of which the petroleum gradually oozing into the well from the adjoining strata is from time to time taken out by buckets attached to a rope wound upon the windlass. Petroleum is also obtained in this way in Moldavia and Galicia along the entire range of the Carpathians. That best suited for refining has a specific gravity of about ·803, but some kinds are thick and much denser, and they are used chiefly for greasing cart-wheels, etc.

Chemically, the materials known as naphtha, petroleum, etc., are all very closely allied, inasmuch as they consist for the most part of homologous liquid and solid hydrocarbons, differing chiefly in density and volatility. The petroleum of America, as well as that of the Carpathians, consists chiefly of substances homologous with marsh gas, and those which have been isolated present the following characters:—

Formula	Specific gravity	Boiling point	Vapour density	Authority
Marsh gas CH_4	—	—	—	Ronalds.
C_2H_6	gaseous.	—	—	
C_3H_8	,,	—	—	
C_4H_{10}	0·600	0°-4°	2·110	
C_5H_{12}	·628	30°	2·538	Pelouze and Cahours.
C_6H_{14}	·669	68°	3·050	
C_7H_{16}	·699	92°-94°	3·616	
C_8H_{18}	·726	116°–118°	4·009	
C_9H_{20}	·741	136°–138°	4·541	
$C_{10}H_{22}$	·757	160°–162°	5·040	
$C_{11}H_{24}$	·766	180°–184°	5·458	
$C_{12}H_{26}$	·776	196°–200°	5·972	
$C_{13}H_{28}$	·792	216°–218°	6·569	
$C_{14}H_{30}$	—	236°–240°	7·019	
$C_{15}H_{32}$	—	255°–260°	7·523	

The various kinds of petroleum also contain other liquid substances of higher boiling point, and of a specific gravity sometimes exceeding ·900. They likewise contain in most instances solid hydrocarbons, varying in amount from 2 to 10 per cent. and upwards, together with pitchy and resinous substances.

The dark coloured oily product obtained by the destructive distillation of wood, peat, or coal and other bituminous minerals and commonly called tar, contains substances identical with those existing in petroleum, together with resinous and pitchy substances, carbolic acid, creasote, nitrogenous bases, etc., the nature and relative proportion of these constituents varying with the kind of material submitted to distillation, and the temperature at which this operation is carried out. The amount of tar obtainable by destructive distillation depends largely upon the amount of hydrogen in the material operated upon, the relative proportion it bears to the carbon, and the amount of oxygen present. The larger the proportion of hydrogen to carbon and the smaller the amount of oxygen, the greater as a rule is the yield of tar, and distillation at a moderate heat only just sufficient for decomposition gives a larger amount of tar than is obtained at a higher temperature, which has the effect of decomposing the oily products to some extent and converting them into permanent gas, while at the same time furnishing tar of a very different character. Thus in the manufacture of illuminating gas by distilling coal at a very high temperature so as to obtain the largest possible amount of gas, the tar obtained is of a totally different nature from that produced at a lower heat, and at the same time a very much smaller amount is obtained.

In the manufacture of hydrocarbon oils, etc., from petroleum, this material is at once submitted to distillation for the purpose of separating the most volatile and the least volatile portions of the petroleum from that portion of the oil which is suitable for burning in lamps; but in manufacturing these products from bituminous minerals it is first necessary to submit the material to destructive distillation and then to operate upon the oily tar thus obtained.

It is of course essential that the materials employed for producing the tar or crude oil should be capable of yielding it in sufficient amount. The most productive minerals are cannel coal, and some kinds of bituminous shale and lignite. Peat has also been used for the purpose, but generally speaking it yields too little to be worth working. The tar obtained by distilling wood is not suitable for the manufacture of hydrocarbon oils, etc., for though it contains these substances together with solid paraffin, they are associated with a very large proportion of resinous impurities that are difficult to separate.

Several varieties of Scotch cannel coal yield a fair amount of crude oil by distillation, but it is chiefly in North Wales that cannel coal has been used for this purpose. That occurring in Flintshire is of three kinds: the curly cannel, which yields about 30 per cent. of crude oil, having a specific gravity ranging from ·875 to ·890, smooth cannel, and bastard cannel, which is more of the nature of shale. The second yields about 16 per cent. of crude oil, of a specific gravity from ·925 to ·940, and the third, which is now most used for distillation, yields from 12 to 15 per cent. of crude oil, having a specific gravity of about ·900. In Scotland extensive beds of bituminous shale occur, associated with coal, and this mineral is largely used for the production of crude oil. The Boghead coal or Torbanehill mineral formerly used for this purpose is now worked out.

These minerals appear to differ from coal chiefly in regard to the proportion of earthy material according to which the applicability of bituminous minerals as fuel is mainly determined.

Lignite or brown coal often yields a considerable amount of tar or crude oil by distillation, especially those kinds in which the ligneous tissues of the plants they originated from have been very considerably altered. On the contrary, those kinds of lignite which have undergone but little alteration yield on distillation products analogous to those obtained from wood.

The lignite, or brown coal, most suitable for the production of oil tar by distillation, occurs in Saxony, and beds varying from half a fathom to four fathoms in thickness extend from the neighbourhood of Weissenfels as far as Zatz. Inferior varieties of the same mineral are obtained also in some other localities.

As regards the chemical composition of this mineral, it is distinguished by the high percentage of hydrogen it contains, amounting sometimes to 11 per cent., while ordinary brown coal does not contain above 6 per cent. The finest kind, which is termed pyropissite, is characterised by a smeary consistence and pale yellow colour; in the fresh state it contains as much as 70 per cent. of water, and when dried it is almost white, earthy, and of light density. This material melts at 150° or 200° to a black vesicular mass; it readily takes fire, and burns with a white smoky flame, emitting a slightly empyreumatic odour; on distillation it yields from 18 to 26 per cent. of an almost colourless oil, that can easily be worked up into marketable products. Generally, the material submitted to distillation for producing oil is less productive, yielding only from 9 to 18 per cent. of oily tar, which contains resinous substances, carbolic acid, creasote, etc.

Peat has been used in several places as a material for the production of hydrocarbon oils and paraffin by destructive distillation, but generally the amount of oil tar obtainable is so small that the working of this material can only be carried on under exceptionally favourable circumstances. The best kinds of dense peat, which approximate in composition to lignite, will yield from 5 to 8 or even 10 per cent. of tar when carefully distilled; but those kinds which are light and spongy, and in which the woody tissue of the mosses they consist of has undergone but little alteration, yield very much less tar by distillation.

Ozokerite or earth wax occurs in various places, associated with coal, but generally in small quantity. In Galicia and in Moldavia there are extensive deposits that are worked as raw material for the manufacture of paraffin and hydrocarbon oils. The colour and other external characters of the mineral vary somewhat, but it is generally brown and compact, less frequently yellow or quite black, and sometimes it has a fibrous or laminated texture. The melting point ranges from 60° to 80°. Another kind is of buttery consistence, and has a greenish brown colour.

Preparation of the Tar or Crude Oil.—This is the most important operation in the manufacture of mineral oil and paraffin from coal, shale, peat, or similar materials, and though the process of destructive distillation appears to be very simple, it is in reality a matter of some considerable difficulty to conduct it in such a manner as to prevent the overheating and decomposition of the oil vapour. A great number of different forms of apparatus have been devised for this purpose.

The construction and arrangement of the horizontal retorts are represented by figs. 455 and 456. The retorts are made of cast iron, they are about 8 or 10 feet long, from 28 to 34 inches wide, and from 9 to 14 inches deep. At the end where

the charge is introduced and the charred residue removed there is a cover (*b b*, fig. 455) fitted so as to be closed air-tight while the distillation is going on. At the

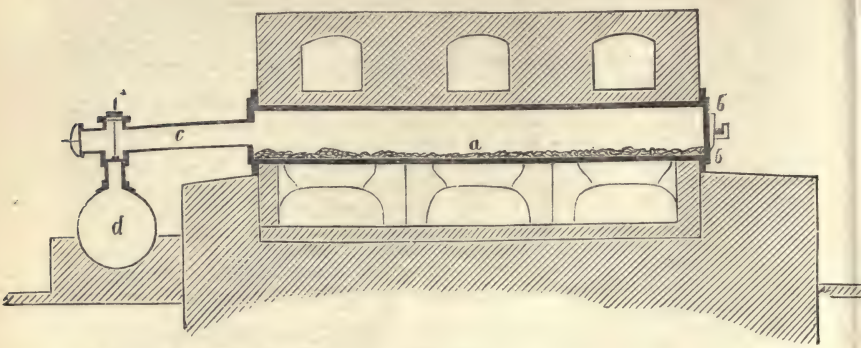


FIG. 455.

other end is a pipe (*c*) for carrying off the product of distillation to a larger pipe (*d*) communicating with the condenser.

A number of these retorts are set together in a row, as shown on a smaller scale in fig. 456, with a furnace (*e*) at one end, and flues (*g g g*) extending beneath the retorts, while the upper parts of the retorts are covered with brickwork (*h h h*), to prevent the oil vapour from being decomposed by the heat of the waste furnace gas passing to the chimney through the flue above the retorts.

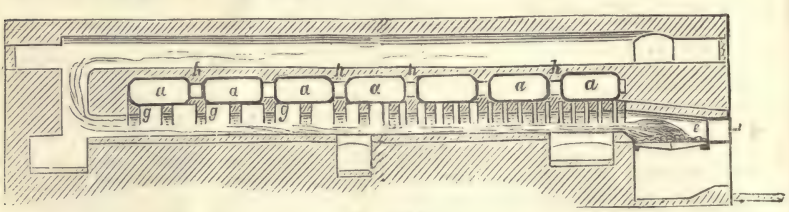


FIG. 456.

The mixture of oil vapour and uncondensable gas discharged from the retorts into the pipe (*d*, fig. 455), passes through a number of iron pipes exposed to the air, or cooled by means of a stream of water running over them, so as to condense the oil which then runs into a reservoir while the uncondensed gas is discharged through an outlet in the system of condensing pipes. In some works this gas is used as fuel, or burnt for producing light.

The retorts are charged through the opening (*b b*), and the material to be distilled is spread over the bottom of each retort in a layer about two inches thick. While the retorts are being charged care must be taken to prevent explosions from taking place, in consequence of the mixture of atmospheric air with the combustible gas and vapour given off. Steam is sometimes driven into the retorts while the distillation is going on, and this practice has the advantage of driving the oil vapour more quickly out of the retorts into the condenser, but it is doubtful if the expense attending the use of steam is not out of proportion to the benefit realised.

The vertical retorts are formed of cast-iron cylinders, set upright in brickwork, as shown in fig. 457. They are from 12 to 16 feet high, and from 3 to 6 feet wide. In some cases these retorts are fitted inside with a system of rings (*a a a*), arranged in such a manner that the coal or other material to be distilled is made to fall down between the edges of these rings and the inside of the cylinder forming the retort, which is heated by the flues (*e e e e*) extending round it and communicating with the furnace (E). At the lower end of the cylinder it is connected with a conical fitting (B B) into which the exhausted coal falls down from the rings (*a a*). The bottom of this cone is connected with the cylindrical box (D), having a damper both at the top and bottom, so that the exhausted coal can be let down into the box and, after closing the damper at *c*, discharged from the box by opening the lower damper. The vapour

given off by the material distilled escapes through the tubes (F G) into a main (H) connected with the condenser.

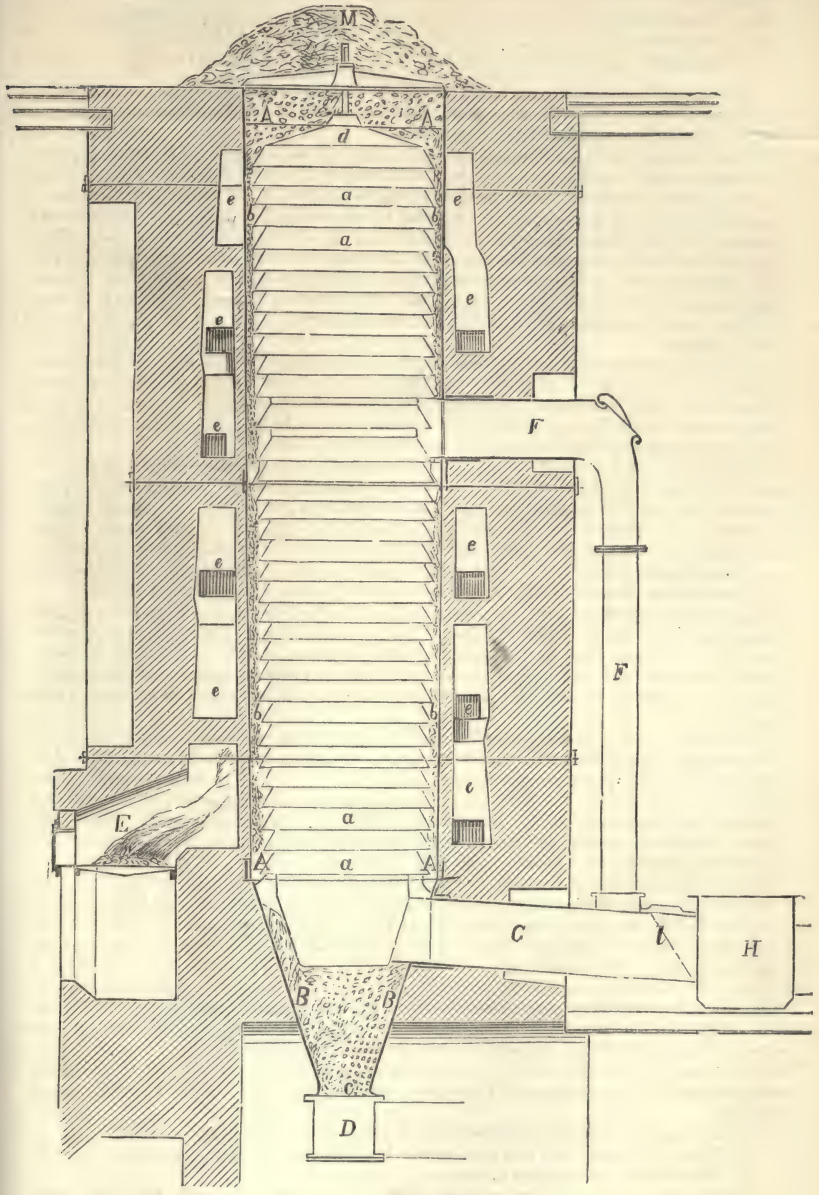


FIG. 457.

The crude oil or tar obtained from bituminous shale or cannel coal is a dark-coloured thick liquid of disagreeable smoky odour, and having a specific gravity ranging from ·840 to ·940; that best suited for refining has a gravity of about ·890.

The tar from brown coal is yellowish brown, having the consistence of butter at the ordinary temperature, and melting at from 25° to 40° into a brown liquid, which

has a dark greenish fluorescence. The specific gravity varies from ·820 to ·870 and upwards, but when it exceeds ·900 the tar is not suitable for the preparation of burning oil. The proportions of the several products obtained from it vary as follows:

Burning oil	28 to 35 per cent.
Heavy oil	10 to 15 ,,
Paraffin	15 to 17 ,,

The tar obtained from peat is almost black, and has a pungent disagreeable smell; at the ordinary temperature it is solid, and has a buttery consistence owing to the large amount of solid paraffin it contains.

The character of the tar or crude oil produced by destructive distillation depends not only upon the nature of the material from which it is obtained, but also to some extent upon the mode in which the distillation is conducted. It is therefore necessary to adapt the retorts to the kind of material to be worked accordingly. The amount furnished by any given material is greater when the distillation is conducted slowly at a low temperature than when the same material is exposed to a higher temperature. The tar produced in vertical cylinders from which the air is excluded is lighter, cleaner, and generally of better quality than that made in horizontal retorts, though a larger yield is obtained with horizontal retorts, and the amount of paraffin in the tar is larger.

For the purpose of preparing oil suitable for burning, etc., the natural petroleum, or the tar or crude oil obtained by distillation of coal, lignite, shale, or other materials, is first submitted to distillation, which has the effect of separating to a great extent the pitchy and resinous substances that give to the materials in their crude state a dark colour, thick consistence, and offensive smell.

At the same time the oil submitted to distillation may be separated into fractions, according to the degrees of volatility and density that the refined products are required to have, and the distillate is run into suitable receivers until only a very small residue remains in the still, which is run out and used for making waggon grease. It is undesirable to continue the distillation until the residue in the still becomes charred, since that causes injury to the still bottom, and trouble in removing the coke formed.

The relative density of the several substances present in petroleum or shale oil, etc., generally bears an inverse proportion to their volatility, those of least density being the most volatile. This relation varies somewhat for different kinds of material, but since in all cases the specific gravity of each successive portion of the oil distilling over is greater as the operation advances, this character affords a means of ascertaining the points at which the distillate should be collected apart from that which has already passed over.

The oil subjected to distillation is thus separated into portions differing in degree of volatility, density, etc., and on this account the operation is termed *fractional distillation*. The most volatile constituents pass over at the commencement, and since their presence in the burning oil would render it too readily inflammable for burning in lamps with safety, this portion of the distillate is rejected until it presents a degree of density such as corresponds with the particular point at which the collection of the oil for burning in lamps may be commenced. This is regulated according to the nature of the material worked and the kind of product required. The oil distilling over after this point has been passed is then run into another receiver, and the distillation is continued until the gradually increasing density of the distillate has again reached a point which indicates that all the oil which can be used for burning in lamps has passed over. What then remains in the still is in many cases drawn off into tanks and distilled separately, but sometimes the distillation is continued until the solidification of the distillate, on cooling, furnishes another indication for collecting the remainder in a separate receiver. When the distillate begins to show signs of solidifying, the water in the condenser tank is allowed to become warm, or, if necessary, it is heated by a jet of steam sufficiently to keep the distillate liquid and prevent the stopping up of the worm, which might give rise to the bursting of the still.

In this way the distilled oil is usually separated into four portions, viz.:

1. The light volatile oil or spirit known by the name of *benzoline*, etc.
2. Oil suitable for burning in lamps.
3. Oil having a specific gravity above ·850, which is used for lubricating machinery, etc.
4. Oil containing a considerable admixture of solid paraffin, which crystallises when the oil is cooled, either at once or after some time.

The distillation of crude petroleum or shale oil is carried out in large vessels made of cast iron or wrought iron, and in some cases superheated steam is forced into the still during the operation. In America cylindrical wrought-iron stills holding 1,600 gallons and upwards are used for distilling petroleum.

The retorts used for distilling shale tar or crude oil are often constructed of large cast-iron flanged pans (A, fig. 458), each capable of holding from $1\frac{1}{2}$ to 3 tons of the oil and forming the body of the retort. The pan is set in brickwork, with flues (*i i*) running round the upper portion, and beneath it is a perforated dome of brickwork through which the flame and hot gas from the furnace (C) pass up round the bottom of the pan (A) before entering the flues (*i i*) by which the upper portion of the pan

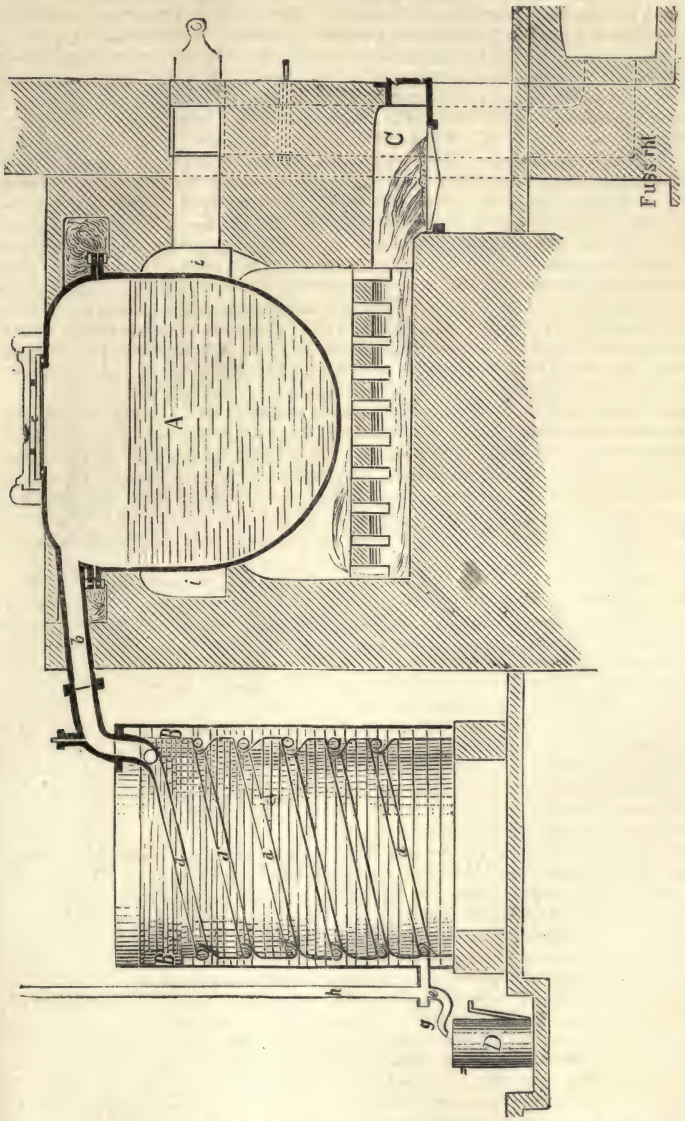


FIG. 458.

is heated. To the flange of the pan is fitted a flanged cover, having at one side a discharge pipe (*b*) through which the vapour is passed to the worm (*d d d*) of the condenser (B B). In the centre of the cover is a manhole (*c*).

The oil condensed in the worm is discharged through the pipe (*e g*) into a receiver (D), and the uncondensable gas escapes through the ascending pipe (*h*).

The several portions of oil obtained by distilling either petroleum or the oily tar

furnished by coal, bituminous shale, or lignite, etc., are generally somewhat coloured, and contain impurities which require to be separated. Thus, for instance, the oil derived from most kinds of tar made by destructive distillation, contains carbolic acid, creasote, and similar substances, for the removal of which the oil is agitated with a strong solution of caustic soda. The products from petroleum rarely require this treatment. When the soda solution used is sufficiently strong the compounds of soda with creasote and carbolic acid, etc., separate as a thick black layer between the layer of oil and the excess of caustic soda solution. After the mixture has been left to settle, the oil is drawn off, washed with water to remove adhering alkali, and then mixed with strong sulphuric acid in the proportion of from two to four per cent. This operation is carried out in large cylindrical vessels furnished with paddles, by means of which the acid can be thoroughly mixed with the oil. By the action of the sulphuric acid the oil acquires a dark brown colour and a considerable quantity of sulphurous oxide is given off. When the mixture is left to settle, a thick tarry liquid of a very dark brown colour is deposited, and the oil, after being drawn off from this deposit of acid tar, is well washed with water, or if necessary with lime water or caustic alkali. With some kinds of oil it is necessary to repeat these operations alternately several times, and sometimes the oil is distilled afterwards. By each treatment of the oil, its colour and smell are gradually removed and, if desirable, it may be rendered quite colourless and almost free from smell. When the oil intended for burning in lamps is distilled a second time, a further quantity of solid paraffin is frequently obtained by collecting the last portions of distillate and leaving them in tanks to crystallise.

The more volatile portion of the distillate from the crude oil is treated in a similar manner with sulphuric acid and alkali, and, if requisite, it is rectified by distillation. It is used for burning in sponge lamps, as a substitute for turpentine and, when highly purified, for removing grease spots from clothes, etc.

The denser portion of the distillate which comes over after the burning oil is seldom sufficiently thick for use as a lubricant for machinery, and it is therefore redistilled and fractionated, the first runnings being added to the bulk of the burning oil before it is treated with chemicals, and the intermediate portion set apart as lubricating oil, while the last portion, containing most of the paraffin dissolved in the oil operated upon, is kept in a cold place until the paraffin crystallises in scales, or it is mixed with the fourth portion of the distillate from the crude oil after that has been treated with acid.

To extract the paraffin from this mixture of heavy oil and paraffin crystals, filter bags are employed in some factories; in others centrifugal machines are used. The scale paraffin thus separated from the greater part of the adhering oil is then wrapped in horsehair cloths and pressed, if necessary with the aid of heat. The pressed mass is then mixed with a quantity of the most volatile oil or spirit and again pressed, this treatment being repeated several times until the paraffin is sufficiently free from colour and smell, and has the requisite melting point.

The refined oil used for burning in lamps varies somewhat in colour, smell, specific gravity, and other physical characters, according to the source from which it has been derived, as well as the care with which it has been prepared, and it is known under a great variety of designations, such as photogen, solar oil, kerosene, paraffin oil, besides other more fanciful names, indicative of a particular make rather than of any essential peculiarity in the oil.

The applicability of these products for burning in lamps is dependent upon the temperatures at which they take fire or give off inflammable vapour. The temperature at which the vapour given off by a sample of oil takes fire by contact with a flame, or the flashing point of the oil, lies a few degrees lower than that at which the oil itself takes fire and continues to burn. In an oil of good quality the flashing point should be above any temperature which the oil will attain during use. According to Chandler, petroleum, during its consumption in glass lamps with a surrounding temperature of 28°–29°, becomes heated after some hours to 30° or 33°; and with a surrounding temperature of 32° or 33½° it becomes heated to 33½° or 36⅔°. In lamps with metal vessels the oil becomes heated to 54°; therefore such lamps are not to be recommended. According to the standard adopted in Great Britain and the United States, the flashing point of oil of good quality should be above 37°·6. Most of the burning oil made from petroleum complies with this requirement, but when it is mixed with oil boiling at a lower temperature it will flash at a much lower temperature, as is the case with inferior kinds of oil met with in commerce containing an admixture of naphtha. An oil flashing at 45° would, according to Chandler, by the addition of 1 per cent. of naphtha, have its flashing point lowered to 39°; by 5 per cent. of naphtha it would be lowered to 28°, and by 20 per cent. to 4°.

Van der Weyde gives the following methods of testing oil for the amount of hydrocarbons having a low boiling point contained in it. A graduated glass tube closed at

one end is filled with the oil to be tested, the open end is closed with the finger and the tube is placed mouth downwards in a vessel of water that is heated to 43–44°. The vapour from the portion volatilised at this temperature then collects in the upper part of the tube and expels a corresponding quantity of oil.

In this country petroleum is defined by Act of Parliament as being any oil which gives off an inflammable vapour at a temperature of less than 37°·6; the method, however, at present in use for determining this point is very imperfect and gives results that cannot be depended upon.

The oil prepared from petroleum is almost colourless, but has a slight bluish fluorescence; it has a specific gravity of about ·810, and when of good quality only a slight and rather aromatic odour. It is now entirely manufactured in America, and is exported thence in very large quantities.

The oil obtained from bituminous shale or from coal is generally of higher specific gravity; it has more colour and a less agreeable smell.

The oil obtained from brown coal tar, and known by the name of solar oil, is almost colourless, with a slight yellowish green or blue fluorescence; its specific gravity is from ·825 to ·835; the lighter and more volatile portion of the oil obtained from this source, and called photogen, has a specific gravity of ·810 or ·825. The temperature at which either of these kinds of oil take fire varies in proportion to the specific gravity as follows:—

	Specific gravity.	Temperature.
Photogen	800	33°
,,	805	37°
,,	808	45°
Solar oil	824	60°
,,	827	68°
,,	830	76°
,,	835	77°
,,	845	92°

Illuminating Gas.—The issue of columns of inflammable vapour from the soil in various parts of the world was known to man many centuries since: at first the phenomenon was the object of fear and superstition, but eventually it was turned to account by practical individuals. In the Middle Ages, the Mahomedans in the district of Baku, south-west of the Caspian Sea, where there was much bituminous oil, collected the vapours streaming from the soil and used them for lighting, brick burning and cooking. Similarly the Chinese of the province of Ou Tong Kias are said to have turned the vapour there exuding through the soil to practical account from the earliest times. The history of the artificial production and application of coal gas for illuminating and heating purposes is much more modern. Nevertheless, long before coal gas was thus used, much was known regarding its properties. As early as 1667 an Englishman, Mr. Thomas Shirley, published in the Philosophical Transactions a communication in which it was stated that the explanation of a burning well at Wigan in Lancashire was to be found not in the water, but in the gas mixed with it, the origin of which gas was attributed to the coal strata lying below. This paper attracted much attention from the scientific world, and gave rise to many attempts to produce combustible gas artificially. In 1685, Professor J. J. Becher published at Frankfort the results of some experiments on the dry distillation of coal, in which he obtained coke, tar, and a luminous combustible gas. Dr. Stephen Hales, in 1726, estimated the amount of gas obtainable from a given weight of Newcastle coal. In 1739, Dr. Clayton, in a paper communicated to the Royal Society, showed that coal gas admitted of storing in bladders, and in 1767 Dr. Watson proved that it retained its inflammable character after passing through water. In 1786 the gas produced by distilling coal at the works of Lord Dundonald, Culross Abbey, was used for lighting.

In 1792, William Murdoch (a Scotchman) experimented, at Redruth in Cornwall, upon the quantities and qualities of the gases furnished by the destructive distillation of various vegetable and animal substances. Subsequently he produced coal gas by heating coal in iron retorts, and used the gas, which was conveyed by pipes, to illuminate his house and offices. The only method of gas purification employed by Murdoch consisted in its passage through water; the use of lime was introduced by Dr. Henry and Dr. Clegg.

In 1798 Murdoch illuminated part of Messrs. Boulton and Watt's foundry in Soho, near Birmingham, with gas; and in 1802 the whole premises were supplied in this way and a number of mills and shops also.

While Murdoch was thus striving to introduce the use of coal gas into England, Lebon was endeavouring to do the same thing for France, although he was anticipated by Murdoch by seven years.

In 1799 Lebon illuminated his house in Paris with coal gas, and caused much astonishment by the proceeding. Mr. Winsor, who was staying at Brunswick at this time, happened to read Lebon's report to the French Institute, and on his return to England did all in his power to introduce the use of coal gas for universal illuminating purposes, but it was a long time before the public prejudice against this innovation could be overcome. Gradually, however, various establishments were lighted by coal gas, and in 1803 the Lyceum Theatre was thus illuminated.

In 1810 Mr. Winsor succeeded in obtaining an Act of Incorporation for the Gas Light and Coke Company, and in the course of a few years a number of other rival companies were started, while the use of coal gas steadily progressed and increased until in fact it became universal.

Paris was first partially lighted with coal gas in 1820; and it was introduced into Germany a few years later. At the present time more than 2,000,000 tons of coal are consumed in gas making for the metropolis, with the production of 14,000,000,000 cubic feet of gas annually. The total consumption of coal in the gas and water works of the United Kingdom amounts annually to more than 7,000,000 tons.

The Chemistry of Gas Manufacture.—When coal is burned in the open air, most of the carbon and hydrogen are burned off as carbonic anhydride and water, while small quantities of ammonia and sulphurous anhydride are produced, being derived from the nitrogenous constituents and the pyrites contained in the coal.

But when coal is strongly heated in closed vessels, in other words when it is submitted to destructive distillation, the decomposition which is effected is quite of a different order. A large amount of permanent or uncondensable gas is formed, and a certain amount of heavier vapour which afterwards, on cooling to normal temperatures, condenses to the liquid or solid state, while a large amount of combustible matter or coke is left behind in the retorts. This gas coke constitutes the bulk of the carbon, and contains, of course, the ash.

The products obtained from cannel coal yielding about 11,000 feet of gas per ton of the density 0·600, are on the average for every 100 lbs. subjected to distillation, about:

Gas	= 22·25 lbs.
Tar	= 8·50 ,,
Ammonia water	= 9·50 ,,
Coke	= 59·75 ,,
	100·00

The gas so produced contains the following constituents; the volume per cent. of each is represented by some determination by the late Dr. Letheby:

	Formulæ.	Volume per cent.
Hydrogen	H	25—50
Light carburetted hydrogen	CH_4	35—52
Olefiant gas	C_2H_4	3—20
Propylene	C_3H_6	
Butylene	C_4H_8	
Acetylene	C_2H_2	?
Carbonic oxide	CO	5—9
Carbon disulphide	CS_2	·004—·04
Carbonic anhydride	CO_2	0—2
Ammonia	NH_3	·00—·06
Aqueous vapour	H_2O	·6—2·5
Oxygen	O	·0—·1
Nitrogen	N	·0—8·0
Benzene and derivatives	C_6H_6	?
Naphthalin	$C_{10}H_8$	?

Dr. Letheby assigned to London gas an average composition as follows:

	Common gas = 12 candles.	Cannel = 20.
Hydrogen	46·0	27·7
Light carburetted hydrogen	39·5	50·0
Condensible hydrocarbons	3·8	13·0
Carbonic oxide	7·5	6·8
,, anhydride	0·6	0·1
Aqueous vapour	2·0	2·0
Oxygen	0·1	0·0
Nitrogen	0·5	0·4

It is now known that, although the illuminating power of gas depends upon the amount

of hydrocarbons it contains, yet it bears more relation to the nature of these constituents than to any relation between the carbon and hydrogen. By long storing or passage through cold pipes, gas loses in illuminating power, owing, no doubt, to the condensation of naphthalin and benzene, and allied or derived substances. Moreover, as olefiant gas is soluble in water, this constituent, which is very serviceable for lighting purposes, is also diminished by storing the gas.

The liquid products furnished by the destructive distillation of coal contain:

Water	H_2O
Carbon disulphide	CS_2
Benzol	C_6H_6
Toluol	C_7H_8
Cumol	C_9H_{12}
Cymol	$C_{10}H_{14}$
Aniline	C_6H_7N
Picoline	C_6H_7N
Leucoline	C_9H_7N
Carbolic acid	C_6H_6O

together with other hydrocarbons of the general formulæ C_nH_{2n}; C_nH_{2n+2}; and C_nH_{2n-6}.

The following substances, which may be obtained in the solid state by refrigeration, are also among the products of coal distillation:

Ammonium carbonate	$2NH_4.CO_3$
,, sulphydrate	NH_4HS
,, sulphite	$2NH_4.SO_3$
,, chloride	NH_4Cl
Paraffin	$C_{20}H_{42}$
Naphthalin	$C_{10}H_8$
Anthracene	$C_{14}H_{10}$
Pyrene	$C_{15}H_4$
Chrysene	$C_{16}H_{12}$

As a matter of fact, the products of the distillation of coal do not range themselves sharply into these three groups. It will be seen that the gas itself generally contains some of the liquid and solid products, while the liquid distillate invariably contains in solution some of the gaseous products.

The relative proportions of permanent gas and condensable solids and liquids, as well as the chemical nature of these products, depend upon the temperature employed in the retorts and the length of time the materials are exposed to the action of heat; the lower the temperature and the more quickly the operation is carried out, the greater is the proportion of solid and liquid products, and *vice versa*. The reason for this is, that more complex substances generally split up into simpler ones on exposure to a high temperature, and the higher this is, the simpler the products. Thus olefiant gas splits up when passed slowly through a red-hot tube into light carburetted hydrogen, hydrogen, and carbon, with loss of illuminating power; and so with other bodies. Therefore, although it is the object of the distillation to get a large yield of permanent gas, it is equally necessary that the illuminating value of the gas should not be destroyed by using too high a temperature or by too slow distillation.

From what has been said, it will be evident that the substances entering into the composition of coal gas may be classed under three headings—illuminants, diluents, and impurities:—

Illuminants.	*Diluents.*	*Impurities.*
Olefiant gas.	Hydrogen.	Sulphuretted hydrogen.
Acetylene.	Light carburetted hydrogen.	Ammonic hydrosulphide.
Propylene.	Carbonic oxide.	,, carbonate.
Butylene.		Carbonic anhydride.
Hydrocarbons of the C_nH_{2n}, C_nH_{2n-6}, C_nH_{2n-12} series		,, disulphide.
		Nitrogen.
		Oxygen.
		Aqueous vapour.

Of the illuminants, taking olefiant gas as a standard, the order in which they stand is directly proportionate to the amount of carbon contained in an equal volume of each, so that naphthalin, the highest, has five times the lighting power of olefiant gas.

The denser members of the group of illuminants are the most readily condensed. From this cause the gas mains frequently become blocked with naphthalin, which has been gradually deposited, owing to the gas having left the holder at a higher temperature than that of the pipes conveying it.

The diluents burn at best with a bluish flame which emits no light; they therefore serve merely to swell the bulk of the gas.

The impurities are not merely useless, but are also noxious or injurious, and require to be removed. Sulphuretted hydrogen rarely occurs in coal gas; but sulphydrate of ammonium and carbon disulphide when present give rise during combustion to sulphurous anhydride; this combining with water and oxygen forms sulphuric acid, which exercises a most deleterious influence upon books and paintings, etc. It is therefore desirable to remove these substances so far as is practicable from coal gas before it is supplied to the consumers.

Carbonic anhydride does not support combustion; it should therefore be removed from coal gas intended for purposes of illumination, inasmuch as 1 per cent. of it depreciates the illuminating power of the gas to the extent of about 6 per cent. The nitrogen present in coal gas is chiefly derived, as is also the oxygen, from the leakage of atmospheric air into the retorts during distillation; since they both reduce the lighting power of gas, it is desirable to avoid their presence as far as possible.

Coal gas being stored over water, becomes necessarily saturated with aqueous vapour, and although the actual amount present is not large, it is objectionable on the same ground as oxygen and nitrogen; moreover, if the gas be used for heating purposes, it is still more objectionable, because it absorbs a certain amount of heat in passing into a more highly attenuated state.

Different kinds of coal used in gas making.—The value of coal for gas making depends upon the amount and nature of the volatile products furnished by heating it, and as bituminous coal excels in these respects, it is the best sort to use for the purpose. Bituminous coal includes the varieties called caking coal, and parrot or cannel coal. Anthracite, which is almost wholly carbon, is quite useless for gas production, and 'steam coal' is unsuitable also in a less degree. The coal used should contain only a small amount of ash, in order that the residual coke may be serviceable as fuel. The absence of sulphur (as pyrites) is also desirable, since the carbon disulphide formed from it in the process of manufacture has afterwards to be removed from the gas produced. The freer coal is from oxygen, the better it is for gas making, since it is only the excess of hydrogen (among other available constituents of coal gas) over the quantity requisite to form water with the oxygen of the coal which is available for lighting purposes.

The Scotch cannel coal yields the largest and richest quantity of illuminating gas, and English cannel ranks next. Newcastle coal is, however, largely used, although its light-producing capacity is only represented by 10, compared with the best Durham at 15, Lesmahago at 25, and Boghead at 40.

The following table illustrates the yield of gas and other products from various coals:—

Name of coal	Produce of one ton of coal				Equivalent of one cubic foot of gas in grains sperm	Consumption per hour to give a light equal to twelve standard candles	Value of the gas from one ton of coals in pounds of sperm
	Cubic feet of gas	Lbs. of coke	Lbs. of tar	Lbs. of ammoniacal liquor			
Boghead Cannel . .	13,334	715	733·3	none	1109	1·3	2057
Newcastle „ . .	9,883	1,426	98·3	60	606	2·37	851
Wigan „ . .	10,850	1,332	218·3	161·6	465·8	3·09	718
Lochgelly „ . .	8,331	1,245	225	340	439	3·28	522
Mixture of $\frac{7}{8}$ Lochgelly and $\frac{1}{8}$ Boghead Cannel .	9,005	1,200	400	170	695	2·07	899
$\frac{9}{10}$ Lochgelly and $\frac{1}{10}$ Boghead Cannel	9,050	1,205	335	290	600	2·4	774
$\frac{11}{12}$ Lochgelly and $\frac{1}{12}$ Boghead Cannel	9,750	1,240	227	270	443	3·25	617
Pelton Main . .	9,500	1,540	112·5	112·5	311	4·7	422
Mixture of $\frac{3}{4}$ Pelton and $\frac{1}{4}$ Boghead Cannel . . .	12,800	1,366	116·6	116·6	553	2·6	1009

The data here given are derived from experiments made by Mr. Barlow, who is

of opinion that coal containing above 30 per cent. of volatile matter requires a higher temperature for distillation.

Newcastle coal gives from 8,000 to 12,500 cubic feet of gas per ton, having a specific gravity ranging between ·398 and ·521.

Parrot or cannel coal gives from 9,000 to 15,000 cubic feet of gas per ton, having a specific gravity ranging between ·460 and ·752.

The coal of Derbyshire, Wales, and Staffordshire, more or less approaches to the Newcastle coal.

The various kinds of coal, especially those of a bituminous nature and intended for gas making, should be protected as far as may be from atmospheric influences. Exposure to rain and sunshine alternately is liable to cause spontaneous combustion; in any case it sets up a rapid oxidation of matter which would otherwise be available for producing gas. This is more especially liable to occur when the coal contains much ferrous sulphide, as this readily takes up oxygen from the air and passes into ferrous sulphate; this oxidation sets up a like action in the coal which is intensified by the heat liberated. A coal may thus in the course of three months lose from these causes as much as 10 per cent. of its productive power.

The following analyses will suffice to show the average composition of coals:

	Per cent. C.	Per cent. H.	Per cent. O.
Boghead cannel	80·35	11·21	6·71
Wigan cannel	85·95	5·71	8·14
Gas coal	88·15	5·26	5·41

Manufacture.—When coal is distilled in close vessels, the elements of which it is composed rearrange themselves, forming a series of bodies the nature of which depends upon a variety of conditions. An excessive temperature splits up the products first formed into more simple ones, such as hydrogen, light carburetted hydrogen, etc., which are valueless for illuminating purposes; on the other hand, if deficient heat be employed, tar results. As it is impossible to keep the contents of the retorts at a uniform temperature throughout, complicated conditions arise, and therefore, besides coal gas, a quantity of tar and ammoniacal compounds pass over, leaving behind in the retorts a highly porous coke. Ordinarily the retorts are charged with from 2 to 4 cwts. of coal, and are maintained as far as possible at a cherry-red heat; at some works, on the introduction of fresh charges of coal, the furnaces are made white hot or nearly so. This operation of distillation takes about four or six hours, during which time the coal yields up all its gas and leaves a saleable coke.

The retorts constitute a most important portion of the apparatus, since upon their construction and arrangement the quality of the gas is largely dependent. They have been the subject of many modifications and improvements, varying most widely in the material of which they are constructed, their form, and their arrangement in the furnace. During the first twenty years iron retorts were always used, but at the present time clay retorts have almost displaced them. A disadvantage attending the use of a retort having a circular transverse section was found to be that the contents were unequally heated, and that in order to reach the central portions of the charge the temperature required to be so high or long continued that it acted injuriously on the gas produced from the coal lying nearer to the circumference. This led to the adoption of the ear-shaped and rectangular retorts (figs. 459 and 460), and afterwards of the ⌂ shaped retorts (figs. 461 and 462). The more rapid decomposition of the coal lying in the angles of these retorts left still much to be desired, and to avoid this inconvenience, the oval retort (fig. 463) is now much used, especially in North Germany. The length of the clay retorts varies ordinarily between 6½ ft. and 10 ft.; their breadth and height average, when of the shape of fig. 460, 19 in. by 12 in.; fig. 461, 32 in. by 6½ in.; fig. 462, from 15 in. by 12 in. to 25 in. by 15 in.; fig. 463, from 17 in. by 12 in. to 23 in. by 39 in.

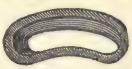

Fig. 459.


Fig. 460.


Fig. 461.


Fig. 462.


Fig. 463.

In the construction of the clay retorts, a mixture of burnt clay with fresh plastic clay is used. The clay must not contain much iron or lime; it must be very plastic and capable of resisting the action of fire, and it should not be too liable to crack or shrink when fired.

The retorts are made with one end closed, and to the other end is fitted a tubular cast-iron mouth piece having the same size and sectional form as the retort, so as to

form a prolongation of it, as shown in fig. 464. This mouth piece (*a*) is connected with the fire-clay retort by means of cement, and is held in its place by screw bolts passing through the flange (*d*) of the mouth piece, and screwed into nuts (*c*) imbedded in the neck of the fire-clay retort. The length of this mouth piece does not require to

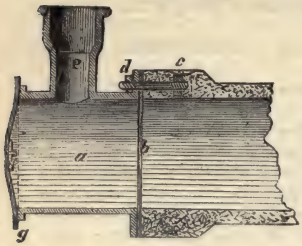


Fig. 464.

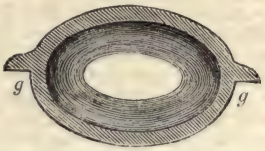


Fig. 465.

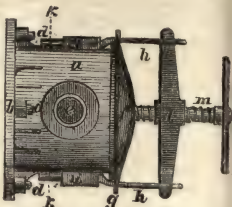


Fig. 466.

be more than enough for attaching the exit pipe (*e*) for the escape of the gas, and that is either cast upon the mouth piece, as shown in fig. 464, or it is fitted on by means of a flange with bolts and nuts. The mouth piece is closed by a lid made of thick iron plate, which fits accurately against the flange (*g*), and, as shown in fig. 465, is furnished with ears or projections (*g g*) at the sides. These ears rest upon two stout iron bars (*h h*, fig. 466), fitted with sockets (*i i*) on the corresponding sides of the mouth piece and held fast by wedges at *k k*. The front ends of these bars have each a slit, into which is inserted the cross bar (*l*), having at the centre a strong screw (*m*) fitted with a handle, and by this means the lid can be pressed tightly against the flange (*y*) of the mouth piece, which is previously smeared with a cement consisting of a mixture of lime and water. A simpler and more convenient arrangement for closing the lid of the retort consists of an eccentric lever attached to a cross bar, as represented by fig. 467.

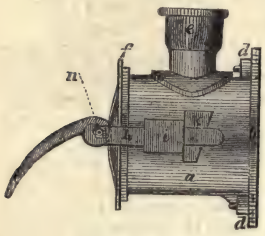


Fig. 467.

The *Retort Furnace* is ordinarily an enclosed arched chamber constructed of fire bricks, in which the retorts are now almost universally arranged in a horizontal position. When iron retorts were used, it was usual to surround them with a casing of fire clay, or to divide them by a closed arch, into which the fire gases passed from behind in order to preserve them from the violent action of the flame from the furnace. Since the general introduction of clay retorts, however, this arrangement has been abandoned. The number of retorts laid in one furnace varies from one to fifteen, according to the size of the establishment.

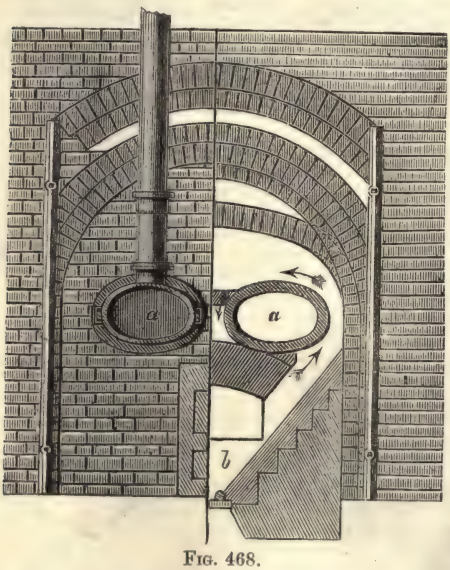


Fig. 468.

Fig. 468 represents a small furnace in which two retorts (*a a*) lie side by side about 3½ feet above the ground, and beneath a flattened arch of about 6 feet span, so as to enclose the retorts as nearly as possible. The fire passes from the hearth right and left of the retorts, and, meeting again above them, is drawn towards the front wall of the furnace, where it descends, and passes along

a horizontal canal, the sides of which are formed by the two retorts; at the back of the furnace the fire gases enter a perpendicular flue controlled by a damper, and through it pass into the chimney.

The bed and interior part of the furnace exposed to the action of the fire are constructed of infusible fire bricks. The outer walls are usually double, and are strengthened by iron stays connecting them with each other and the retort benches. By this means not only is additional solidity of the building secured, but the exterior walls assist in retaining the heat and preventing undue loss by radiation. When coke is used for fuel, the fireplace is made comparatively deep; the air entering from beneath has then to pass through a considerable depth of fuel, a condition which favours the formation of carbonic oxide and the consequent production of a flame of great heating power. An ash pan beneath the fire grate is kept partly filled with water, in which the hot ashes falling are extinguished, whilst the resulting steam tends to lower the temperature of the furnace bars, and passing upwards through the incandescent fuel is decomposed with the formation of carbonic oxide and hydrogen.

Notwithstanding all precautions taken for the equal heating of the retorts, some of them are always exposed to a greater heat than the others; consequently they are

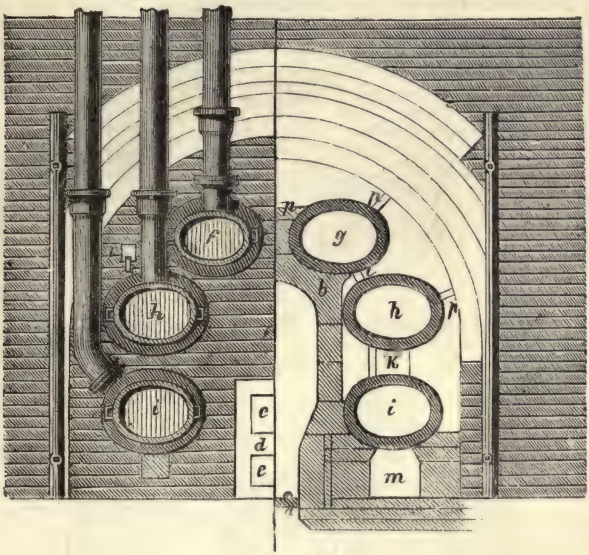


Fig. 469.

destroyed more quickly, and require to be thrown out of action until the re-setting of the entire bench. Those retorts that are exposed to the greatest heat also require to be re-charged more frequently than the others, to prevent the contamination of the gas with sulphur to a greater extent than is the case when the coal is not heated strongly for a long time; when the distillation is not carried too far much of the sulphur is left in the residual coke. In charging the retorts, the coals are placed as far back in the retort as possible, by means of a sheet-iron scoop. At the same time the mouth of the exit pipe is closed to prevent either gas flowing back into the retort, or atmospheric air, carbonic dioxide, etc., being drawn into the pipe from the furnace.

Fig. 469 shows the arrangement in a furnace containing six retorts capable of producing with retorts of the ordinary dimensions 50,000 cubic feet of gas in twenty-four hours. An important point to be considered is that there should be perfect combustion of the fuel in the furnace. The retorts are therefore arranged in the form of an arch around the hearth. At the grate (*a*) the fire hearth is about 1 foot wide; at a distance of 1 foot higher it widens to 2 feet; it then rises about 1½ feet, and is closed in by a brick arch (*b*). The fuel, usually coke produced in previous operations, is introduced through the furnace door (*c*); this and the ash pit door (*e*) are set in a cast-iron frame (*d*), securely bolted into the front wall of the furnace. The flame rising from the hearth is hindered from passing between the retorts (*g h i*), by barriers of brick (*k l*). It therefore rises between the arch (*b*) and the top retorts (*f g*) to the crown of the vault, then spreads right and left, and descends between the

outer side of the retorts and the wall of the vault to the level of the bottom of the lowest retorts (*i i*); the fire gases here enter a passage (*m*) running under the entire length of these retorts, which acts as a draught, through which they are drawn at a velocity regulated by a damper into the chimney.

The same advantages are said to be afforded by a furnace containing seven retorts,

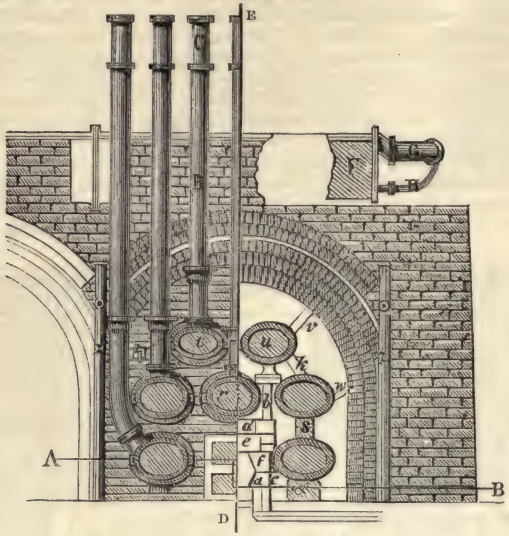


FIG. 470.

the same proportions being maintained. The arrangement is represented in figs. 470, 471, and 472; fig. 470 being a front view, fig. 471 a horizontal section at the line A B, and fig. 472 a vertical section at the line E D.

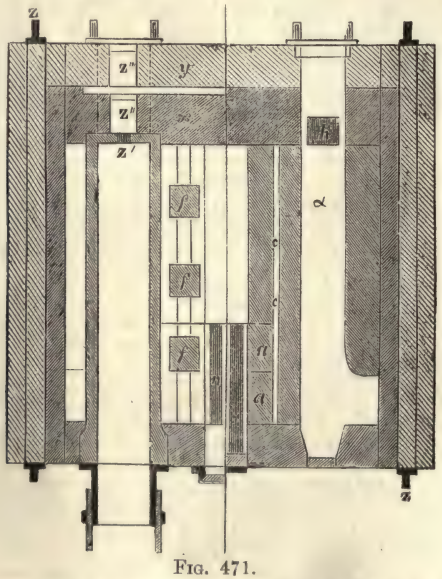


FIG. 471.

The seventh retort (*r*) is here laid over the furnace formed by the fire bricks (*a f e*); *d* is a plate which supports the middle retort, and at the same time protects it from the play of the fire; *o* is the opening for the introduction of fuel; *p* the opening for

the ash pit; *g g* the corresponding doors. Under the grate is a cast-iron water tank (*q*), where water is always kept, in which falling pieces of coke are extinguished and at the same time steam is produced that exercises a cooling action on the fire bars. The fire plays round the middle retort (*r*), and being prevented by the fire-brick partitions (*k s*) from passing out sideways, rises as in the six retort furnace, between the top retorts (*t u*), descends into the flues (*a* and *h*), and through them into the chimney; *v* and *w* are the stays of the retorts against the sides of the furnace; *b* and *e* brickwork supports for retort *u*; *l* a swing flap for observing the heat of the oven. Besides the interior supports, the retorts rest at either end in the front and back walls of the furnace. The front wall is built of fire bricks, 9 inches thick; the back wall is double (*x y*), being separated by a stratum of air that acts as a non-conductor of the heat. The entire furnace is enclosed above by five arches, the three inner ones lying close on one another, being built with fire bricks; the other two, separated from them by a small interval, being built with ordinary bricks. Above the outermost arch there are frequently two layers of plaster to retard the radiation of heat. In fig. 472 is shown the mouth of the retort (A), which projects beyond the front wall, and is fitted with a vertical cast-iron pipe (B), through which the whole products of the distillation ascend to the hydraulic main (F). When the coal has been introduced into the retort, the mouth is closed with a lid luted with fire clay, or some other suitable material, and fastened with a screw or lever as already described.

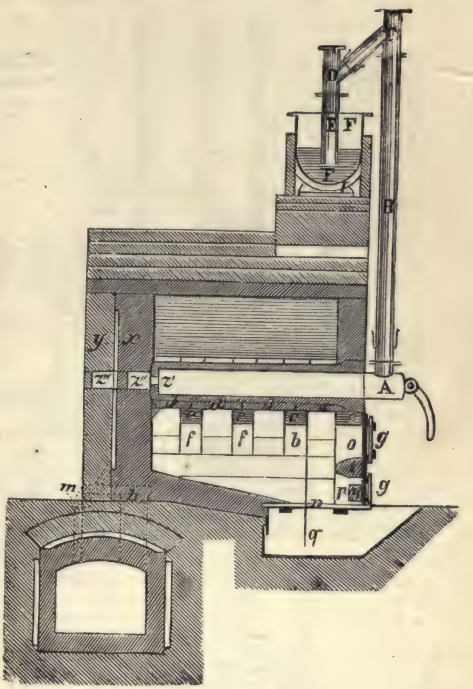


FIG. 472.

The hydraulic main (fig. 472, F), into which the gas passes from the ascension pipes (BC), is a horizontal iron trough that is at first half filled with water, into which the continuations (D E) of the ascension pipes dip. The gas bubbles through, but a part of the tar and ammoniacal liquor is condensed, and this soon displaces the water, and in its turn, when it has reached a certain level, flows over into the tar well. The hydraulic main acts therefore as a water joint, and effects a partial condensation and purification.

Retorts are usually set in groups of three, five, seven, eight, or nine to a bench, each setting being heated by a separate fire regulated by independent dampers, but connected with a common flue. They are either single, when they are about 8½ feet long, and closed at one end, the other being fitted with the mouth piece; or they are double, in which case they are 18 or 20 feet long, and have a mouth piece at each end. Single clay retorts are usually in one piece, and to strengthen them they are set in a casing of fire bricks; but the double retorts may be either built in sections or constructed entirely of fire bricks. After a time the retorts become coated with a very hard deposit of carbon, and require to be scurfed. This is done by removing the deposit with a hammer and chisel, or when it has become very thick and hard, by admitting atmospheric air to the retort and allowing the carbon to burn away until the crust is sufficiently thin to be easily removed.

The quantity of fuel consumed varies greatly, and depends especially upon the quality of the coke; usually it is calculated to use one third of the coke drawn from the retorts in feeding the fire. This quantity, however, can be reduced if air pre-

viously heated be introduced under the fire grate. This passes to and fro through narrow channels along the length of the flue, and increases by its heat the effect of the combustion. Thus the seven retort furnace represented in fig. 470 would require on the average 236 parts of coke for the distillation of 1,000 parts of coal; whilst a furnace with nine retorts and double fires, as represented in fig. 473, in which this plan is adopted, would only require 213 parts of coke to do the same amount of work.

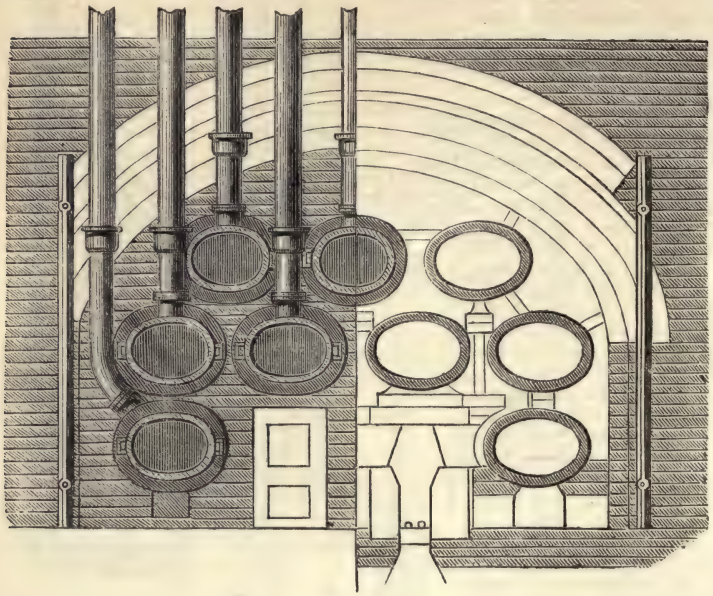


FIG. 473.

From the hydraulic main the gas passes to the condenser, which it enters at a temperature of about 70°, at which it still retains a considerable quantity of tarry and aqueous vapour. In the smaller gasworks, the condenser used for the separation of these impurities consists of a series of pipes kept cool by exposure to the air. Such an arrangement is shown in fig. 474, a ground plan in fig. 475. The pipes are supported upon and open into a chamber (*a a*) for the reception of the condensation products, the chamber being divided into several compartments by a series of partitions reaching not quite to the bottom. The gas entering at s into the first compartment (1) rises through the pipe opening into it (*b*), passes through the cross-pipe (*e*), and descends by the opposite pipe (*c*) into the second compartment (2), then rises through the third pipe (3), and passes through another cross pipe corresponding to *e*, and so on through the whole series of pipes, and escapes through the outlet (A). The condensation products

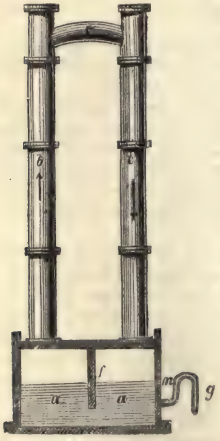


FIG. 474.

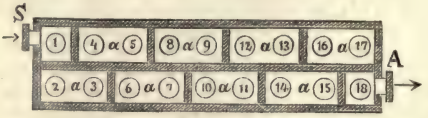


FIG. 475.

escape through an overflow pipe (*g*), arranged so as to maintain a constant level within the chamber above the communication between the several compartments.

In large gas works, where it would be difficult to obtain a sufficient condensation by the action of atmospheric air alone, cold water is also used; the arrangement is shown in fig. 476. In this condenser the gas passes through three upright tubes (A B C) about 3 feet in diameter and 16 feet in height, each containing seven iron 2½ inch pipes (*c e e*), arranged as shown in (C B), in which water circulates in a contrary direction to the gas. The gas enters at *a*, passes through the tubes (A B C) and the connecting pipes (*b c*) successively, to the exit valve (*d*). The cold water enters through a pipe (*f*), at a point below the third tube (C), ascends through it and passes through the connecting pipe (*g*), then descends through the second tube (B) and the connecting pipe (B), and finally rises through the first tube (A), escaping at the top. The temperature is shown by a thermometer in each tube (*i i i*), and the flow of water is so regulated that the gas leaves the condenser at about 15°. The condensation products run from A through *b*, and then pass with those from *e* into a 2 inch pipe (*k*), onward to the tar reservoir (*l*). Should any defect occur in the apparatus, the valves at the entry (*a*) and exit (*d*) are closed, and the gas passes directly from the supply pipe through a branch (*a δ*) communicating directly with the discharge pipe, the valve controlling it (*β*) being opened.

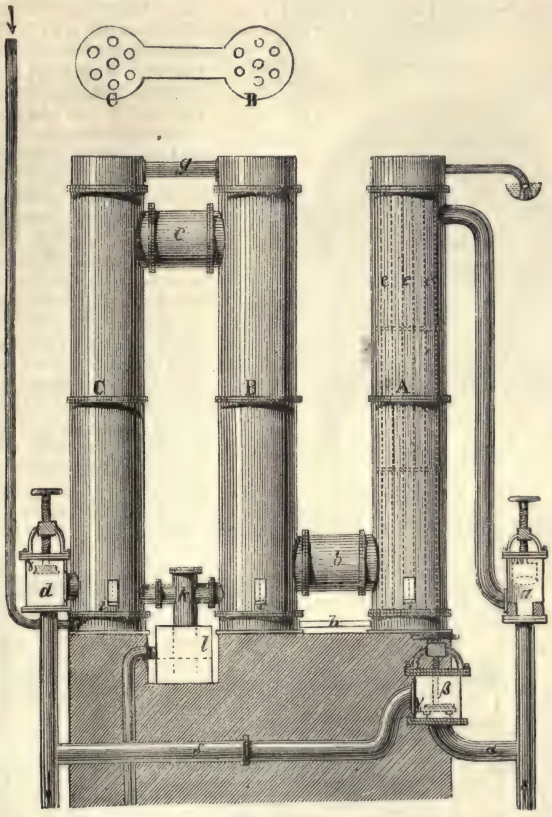


FIG. 476.

The object of the condenser is to effect the cooling of the gas to the atmospheric temperature, and at the same time the separation of suspended water and tar. In many cases this result can be produced by making the gas pass up and down through a few pairs of upright pipes of the kind above described, but several improved arrangements have been introduced with the object of offering a greater surface of contact between the gas and the cooling medium. In Kirkham and Wright's condensers this has been done by making the gas traverse an annular space formed by two concentric cylinders, and the gas passing through this annular space was thus cooled both from

within and from without by the cold air passing up through the inner cylinder as well as over the surface of the outer cylinder. These annular condenser tubes are connected by smaller pipes, which convey the gas from the bottom of one condensing cylinder to the top of the adjoining one, so that in all cases the gas passes from the top to the bottom of the condensing cylinders in a direction contrary to that of the current of air by which it is cooled. An area of six to ten square feet of condensing surface is considered to be necessary for each thousand cubic feet of gas made during twenty-four hours.

Passing from the condenser the gas reaches the exhauster, an apparatus having for its object the withdrawal of the gas from the retorts as soon as it is produced, and its propulsion through the various purifying materials to the gas holder. The reason for drawing off the gas from the retorts as quickly as possible is to avoid its being subjected to pressure, which if it be at all considerable at a given temperature exercises upon the gas the same effect as a much higher temperature without pressure, namely, the splitting up of condensable hydrocarbons into non-illuminants, which has the effect of not only reducing the amount of gas obtained, but also of lessening the illuminating power of the gas, and causing a deposition of carbon upon the interior surface of the retorts.

A rotary exhauster is shown in figs. 477 and 478. This consists of a cylindrical case (A) in which a smaller cylinder (B) is rotated eccentrically by a driving shaft making 60 to 100 revolutions a minute. At a right angle with the shaft are two sliding plates working in a groove upon one another in such a manner that whatever the position of the inner cylinder the space of the outer frame is divided into two parts. In the position shown in the sketch the entrance and exit are closed, and the upper space is filled with gas. When the cylinder is rotated in the direction of the arrows, the left-hand slide is pushed in, whilst the right-hand one slides forward so as to remain in contact with the side of the frame. At the same time the opening of the exit pipe becomes uncovered, and the gas in the upper part of the frame is by the eccentric action of the inner cylinder driven forward by the right-hand slide into the pipes. When the revolution is half completed, the inlet pipe in its turn becomes uncovered, and a fresh quantity of gas enters

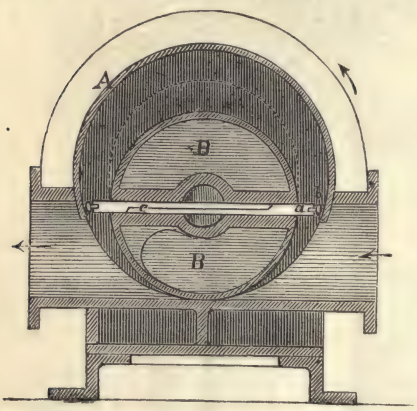


FIG. 477.

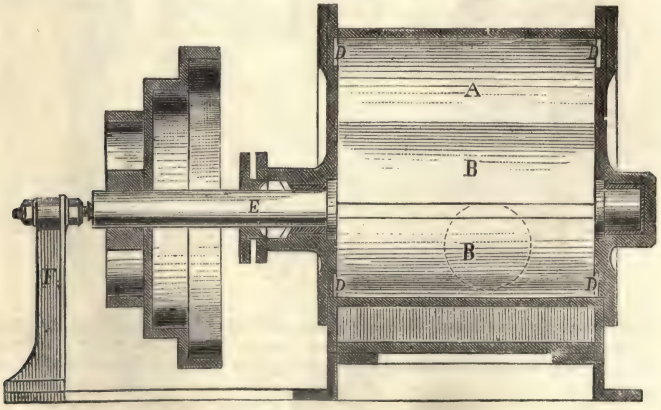


FIG. 478.

the chamber. In this manner, exhaustion on the one side and pressure on the other are constantly kept up.

A machine of this kind about four feet in diameter is capable of passing through it about 150,000 cubic feet of gas per hour, according to the rate at which it is driven.

A piston exhauster is represented in fig. 479, which resembles a steam engine in its action. The gas entering at the inlet pipe (A) passes according to the position of the slide (C) in the slide chamber (B B), into a vertical cylinder through either of two channels, one (D) above the piston (G), the other (E) below it. When the piston (G) is at the bottom of the cylinder, the slide (C) is in the position represented in the figure, and the inlet pipe (A) and the two channels (D and E) are shut off from each other. Directly the movement of the piston is reversed the slide slips downwards, and communication is established between the inlet pipe (A) and the lower channel (E), and between the upper channel (D) and the slide chamber (B), so that the ascending piston drives the gas contained in the upper part of the cylinder forward through the upper channel (D) and the chamber (B), whilst a fresh quantity of gas is drawn in from the inlet pipe (A) through the lower channel (E) to fill the vacuum created. When the piston reaches the top of the cylinder, communication is again shut off, and when it descends the conditions are reversed, the gas being drawn in through the upper channel and expelled through the lower one.

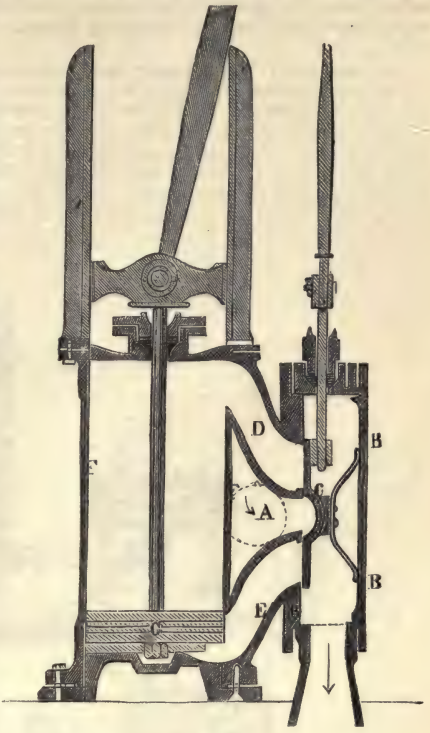


FIG. 479.

In order to avoid the danger of explosion that would result from the inflow of air in consequence of the quantity of gas produced in the retorts being sometimes unequal to the action of the exhauster, the supply of gas is controlled by a regulator.

The construction of the regulator used for this purpose is represented by fig. 480. The cylindrical vessel (A) is partly filled with tar, and the cylindrical bell (B), furnished with a hollow ring (C) internally, dips into the tar contained in the vessel (A), and is kept down to the required level by weights (P) slipped on to a pin attached to the top. Beneath this bell are fixed two concentric pipes (S S and D); the external wider tube (S) branches from the main through which the gas is sucked from the scrubber; the inner tube (D) branches from the main through which the gas drawn out by the exhausters is forced into the purifiers. In the former there is consequently pressure, and in the latter rarefaction, of the gas. The exhauster and regulator are sometimes placed immediately after the hydraulic main or after the condenser, but in that case the separation of tar and ammoniacal water causes destruction of the metal or hinders the action of the regulator. When the dip pipes of the retort are immersed about an inch, it is necessary that the exhauster should be driven in such a way as to produce a rarefaction equal to nearly half an inch in the suction tube. This is the normal condition of the regulator, which is adjusted in such a way that a conical valve (F) attached to the cover of the bell closes the outlet of the tube (D). So soon as the

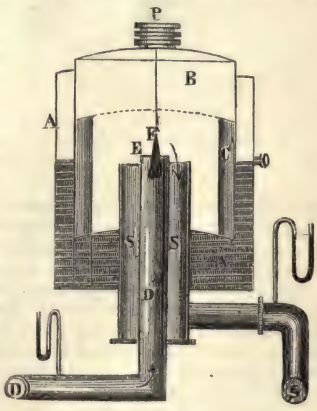
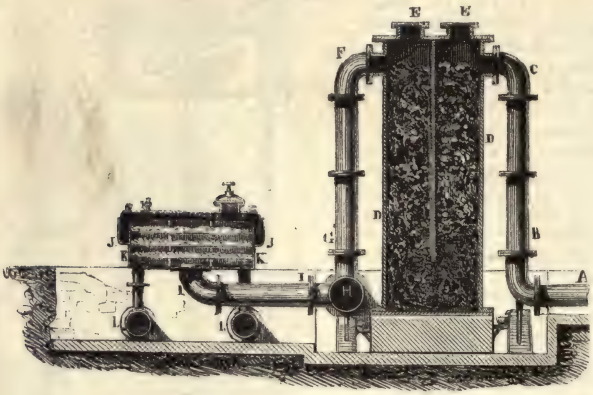


FIG. 480.

rarefaction becomes greater the regulator begins to act, and by sinking opens the conical valve (F), admitting gas into the bell and reducing the rarefaction. As this condition recurs at frequent intervals, a trembling motion of the bell is produced, which admits of the action of the apparatus being observed. When the speed of the exhauster is too great for the rate at which the gas is being produced, the gas which has already been exhausted and driven to the purifiers escapes again into the suction tube.

In some works the gas is next made to bubble up through water in the washers; in others it passes directly to the scrubber. This is constructed on the same principle as Gossage's towers for the condensation of hydrochloric acid gas, and is represented in figs. 481 and 482. It consists of one or more cast-iron cylinders or square chambers (D D), the interior of which is separated into two parts by a partition reaching from the top almost to the bottom. These compartments are filled almost to the lids with a porous material, usually coke, the extensive surface of which withdraws from the gas a considerable portion of the ammoniacal compounds, and nearly

FIG. 481.



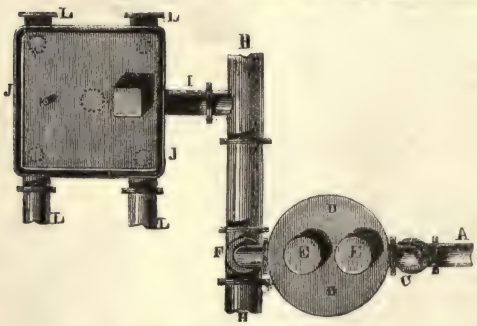


FIG. 482.

all the remaining tar. This effect is increased by keeping the coke moistened with dilute ammonia liquor from the hydraulic main, which absorbs sulphuretted hydrogen, and the resulting ammonium sulphydrate combines with carbon disulphide. The coke saturated with tar is afterwards used for heating the retorts. The gas enters the right-hand compartment through a pipe (A B C), passes through the coke to the bottom, rises through that in the left-hand compartment and escapes through another pipe (F G). In cases where particles of tar adhere very pertinaciously to the gas, or where it is important to remove the last traces of it, the scrubber is combined with shallow cast-iron chambers (K) having a large horizontal area, in which lie wooden hurdles covered with a loose layer of coke refuse, broken clay retorts, etc. The last traces of tar condense here, and the gas entering from H and J, after passing through three layers of hurdles in the boxes (K), leaves through the pipe (L) for the purifiers, absolutely free from tar.

The gas should leave the condenser at a low temperature, for the cooler the gas as it enters the scrubbers, the greater is the purification they effect. At this stage all the remaining ammonia, mainly in combination with carbonic acid and sulphuretted hydrogen, is removed, and the solution thus obtained is used for the manufacture of ammoniacal salts. The average amount of ammoniacal liquor thus obtained from the scrubbers and condensers is estimated at about 20 to 25 gallons of 10 oz. liquor per ton of coal.

Besides these constituents of gas liquor, there are many others, including sulphurous acid, sulphuric acid, cyanic acid, sulphocyanic acid, and hyposulphurous acid, and a small quantity of free ammonia.

Up to this point, with the partial exception of the scrubber, the purification of the gas has been mechanical. Thus the gas before reaching the condenser deposits in the hydraulic main some of the heavier tarry matter and water containing ammonia in solution. The amount of liquid tar deposited in the condenser is greater, and the ammonia liquor amounts to about 9 gallons of 6 or 7 oz. strength to the ton of coal; this represents about one fourth of the total ammonia present in unpurified gas.

Sometimes dilute sulphuric acid is employed in the washers to fix the ammonia, but this plan is only used in certain small works; it has the advantage of producing sulphate of ammonia direct, but the product requires purification by recrystallisation before it is ready for the market.

Here and there sulphate of iron is employed in the purifiers for the removal of ammonia and sulphuretted hydrogen; its use is based upon the following reactions:

$$(1)\ FeSO_4 + 2NH_4HO = 2NH_4.SO_4 + FeO + H_2O$$
$$(2)\ FeO + H_2S = FeS + H_2O$$

Ordinarily, however, the ammonia is removed from coal gas by the process first described. Its removal from coal gas is desirable not only because of the value of ammonia, but also on sanitary grounds. During combustion of the gas any ammonia present is liable to conversion by oxidation into nitrous compounds, and these are not only deleterious to health, but act injuriously on brass and other metal fittings.

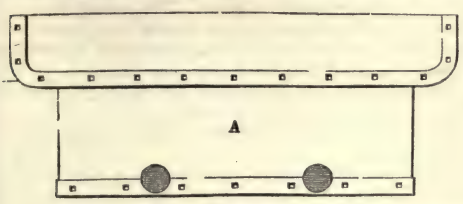


FIG. 483.

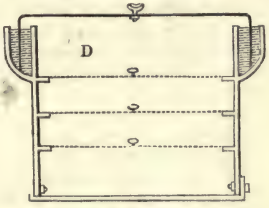


FIG. 484.

The impurities still requiring to be removed from the gas before it is fit for use are carbonic dioxide and sulphuretted hydrogen.

To remove the carbonic acid from gas nothing is more efficient than lime, which also absorbs the sulphuretted hydrogen when used either in the state of milk of lime or simply slaked.

Although wet lime is more effectual as a purifier than dry lime, its use is open to many objections, so that now, if lime is used at all, it is almost invariably used in the dry state.

	Cubic feet of Sulphuretted hydrogen		Cubic feet of Carbonic acid
1lb. of quick lime in the dry state absorbs	6·78	and	3·39
1lb. of „ „ wet „ „	6·78	and	6·78

The vessels in which the gas is submitted to the action of dry lime consist of sheet-iron boxes fitted with a water joint, into which the cover dips and prevents escape of gas, as shown in figs. 483, 484 and 485, which represent an elevation, and two sections of one of these purifiers. The gas enters at the bottom, and passes up through the purifying material spread upon the shelves on one side of the central partition, and then down through the shelves on the opposite side to an exit pipe at the bottom (fig. 483).

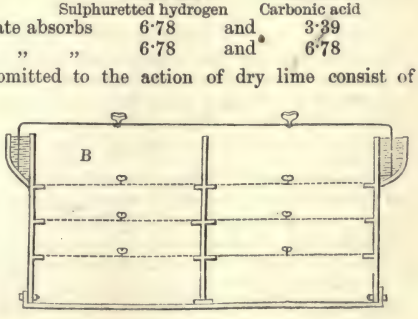


FIG. 485.

Several of these chambers are connected together, and the gas is made to pass through them successively. A usual arrangement is represented by fig. 486, where four chambers (R I. to R IV.) are connected together in such a manner that,

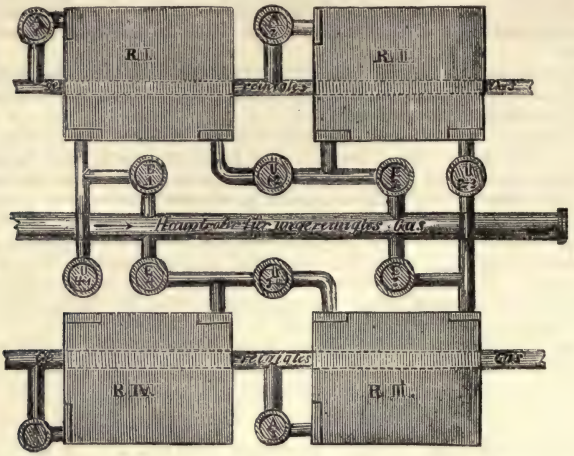


FIG. 486.

while any three of them are being used the gas is shut off from the fourth, in order to remove the exhausted purifying material and replace it with a fresh supply. The gas is admitted to these chambers from the main through which the unpurified gas passes by opening the valves (E_1 to E_4) in the connecting pipes. The valves (U_1 to U_2, etc.) are for connecting the several chambers with each other as may be required, and the valves (A_1 to A_4) are for letting out the purified gas. If the chamber (R II.) is to be cleared out and charged with fresh material, the gas enters the chamber (R III.) through the valve (E_3), passes through U_3 to the chamber R IV., through U_4 to the chamber R_1, and then through the valve A_1 to the main for purified gas.

Another material used for purifying gas is hydrated ferric oxide, which absorbs the sulphuretted hydrogen very effectually.

In the gas purifiers oxide of iron is sometimes used alone; but this plan, while it effectually removes the sulphuretted hydrogen and admits of constant regeneration of the purifying material and utilisation of the sulphur, has the disadvantage of allowing the carbonic anhydride present in the gas to escape removal. On the other hand, slaked or moist lime absorbs both impurities, but the sulphur cannot be utilised.

A mixture of slaked lime and peroxide of iron is still largely used, although more generally peroxide of iron is used without lime, but mixed with sawdust to give it porosity. Peroxide of iron occurs in a hydrated state naturally as bog iron ochre, and this constitutes the material usually employed in gas purification. The credit of having brought this process to perfection is due to Mr. Hills. To carry it into effect, the gas to be purified is passed through the mixture of ferric oxide and sawdust for a period of 18 hours, and by the reaction of the ferric oxide with the sulphuretted hydrogen ferrous sulphide and water are formed, while sulphur is liberated:

$$Fe_2O_3 + 3H_2S = 2FeS + S + 3H_2O,$$

after which the mixture is subjected to a current of air produced by a fanner during a period of three hours. In this way the ferrous sulphide formed by the action of the sulphuretted hydrogen upon the oxide of iron undergoes oxidation, giving once more ferric oxide and free sulphur, thus:—

$$2FeS + O_3 = Fe_2O_3 + S_2$$

These processes are repeated and continued until the product contains as much as 40 per cent. of sulphur, and 1 ton of this mixture is said to yield, when burnt for sulphuric acid making, $1\frac{1}{4}$ tons of hydrated sulphuric acid. About once a month a certain amount of the oxide of iron has to be replaced, owing to the bottom layer becoming clogged with tar; but the loss thus occasioned is not very great.

In addition to sulphuretted hydrogen and carbonic anhydride, there are other impurities which it is desirable to remove from coal gas, notably carbon disulphide and sulphuretted hydrocarbons; all of which when burnt in the air form sulphurous

acid. Mr. Wright has ascertained that if a moderate temperature be employed in distilling the coal used for gas-producing, the amount of these substances is reduced very considerably, but this is a remedy not likely to be adopted to any great extent. It is therefore important to find other means of obviating this evil.

Mr. Harcourt has attempted to meet it by a process which consists in passing the gas through heated tubes containing lime or other substance, when sulphuretted hydrogen is produced by decomposition of the bisulphide of carbon. This action is not peculiar to lime; almost any material will act like it; hence it appears to result from physical rather than chemical causes. When the process was used on a large scale, however, it was found that after a time the catalytic substance became inactive, and the difficulty thus experienced has not yet been surmounted. If it could be, it would be easy to apply this process to coal gas before it passes to the purifiers which remove the sulphuretted hydrogen; the problem of removing the bisulphide of carbon from coal gas must therefore still be regarded as unsolved.

The following table, representing the composition of the gas taken from different parts of the apparatus, will serve to show the effect produced by different stages of the purification:—

	From condenser	From scrubber	From washer	From purifiers	
Hydrogen	37·97	37·97	37·97	37·97	37·97
Marsh gas	39·78	38·81	38·48	40·29	39·37
Carbonic oxide	7·31	7·15	7·11	3·93	3·97
Heavy hydrocarbons	4·19	4·66	4·46	4·66	4·29
Nitrogen	4·81	4·99	6·89	7·86	9·99
Oxygen	0·31	0·47	0·15	0·48	0·61
Carbonic dioxide	3·72	3·87	3·39	3·33	0·41
Sulphuretted hydrogen	1·06	1·47	0·56	0·36	—
Ammonia	0·95	0·54	—	—	—

These quantities, in parts by measure in 1,000 cubic feet, are as follow:—

	From condenser	From scrubber	From washer	From purifiers	
Hydrogen	380	380	380	380	380
Marsh gas	390	388	384	403	394
Carbonic oxide	72	71	71	39	30
Heavy hydrocarbons	42	46	45	46	43
Nitrogen	48	50	69	79	100
Oxygen	3	5	2	5	6
Carbonic dioxide	40	39	34	33	4
Sulphuretted hydrogen	15	15	5	3	—
Ammonia	10	5	—	—	—
	1000	999	990	988	966

After leaving the purifiers, the preparation of the gas is complete, and it only has to pass through the station meter where the daily make is registered, from whence it passes on to the gas holder, where it is stored.

As supplied to consumers, coal gas has a composition shown by the following table, giving the average composition of coal gas supplied by the companies named:—

	Great Central	Imperial	Chartered
Illuminating hydrocarbons	3·56	3·67	3·53
Marsh gas	35·28	40·66	35·26
Hydrogen	51·24	41·15	51·80
Carbonic oxide	7·40	8·02	8·95
Carbonic acid	0·28	0·29	—
Nitrogen	1·80	5·01	0·38
Oxygen	0·44	1·20	0·08
	100·00	100·00	100·00

After being measured by passing through the station meter, the gas reaches the gas holder, where it is stored up until required. The gas holder consists essentially

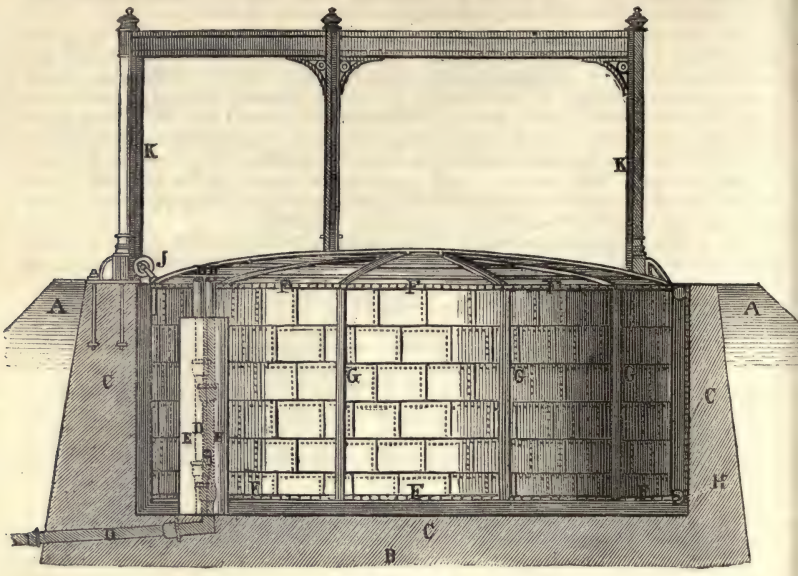


FIG. 487.

of a cylindrical vessel made of sheet iron, covered at the top and open at the bottom. This is placed in a sunk pit, lined with masonry (C C C), of a somewhat greater diameter than the cylinders, and capable of being filled with water. Such a gas holder is represented in fig. 487. Into this basin project several inches above the level of the water, and supported by a wall (E), the inlet and outlet pipes (D). As there is a liability of condensed water, tar, etc., collecting in the lower part of these pipes, they slope slightly to the outside of the basin, where the accumulated substances can be removed by a hand-pump.

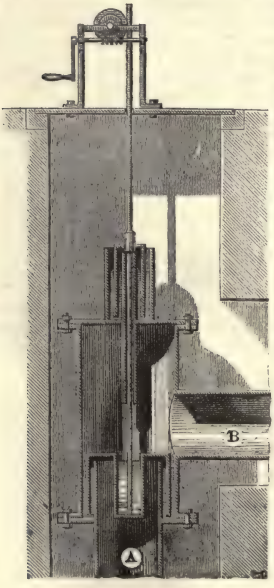


FIG. 488.

The passage of the gas in either of the tubes can be stopped by a valve of the kind represented in fig. 488. This valve consists of a bell-shaped cover fitting over the end of the inlet pipe (A), and dipping into tar or water retained round the end of the pipe by an outer casing, to the side of which the outlet pipe (B) is attached. While this bell-shaped cover is in the position shown in the drawing, the valve is closed, but when it is raised by means of the connecting rod and windlass above, communication is established between the inlet and outlet pipes.

The upper and lower edges of the gas holder are strengthened by wrought iron rings (F F F, fig. 487), and the sides are strengthened by vertical ribs (G G) of angle iron. The cylinder is capable of being raised as it becomes filled with gas, and the rollers (J J) attached to the upper ring, run upon guide bars attached to the pillars (K K).

The Meter.—Before the gas is delivered for consumption, it is requisite it should be measured. The metres employed for this purpose are distinguished as wet meters and dry meters, and they are fixed to the supply pipe in each house. The construction

of a wet meter is represented by fig. 489. The gas enters through the pipe (*a*) into the upper part (*b*) of the chamber (A A), and passes through the hole (*e*) into the lower

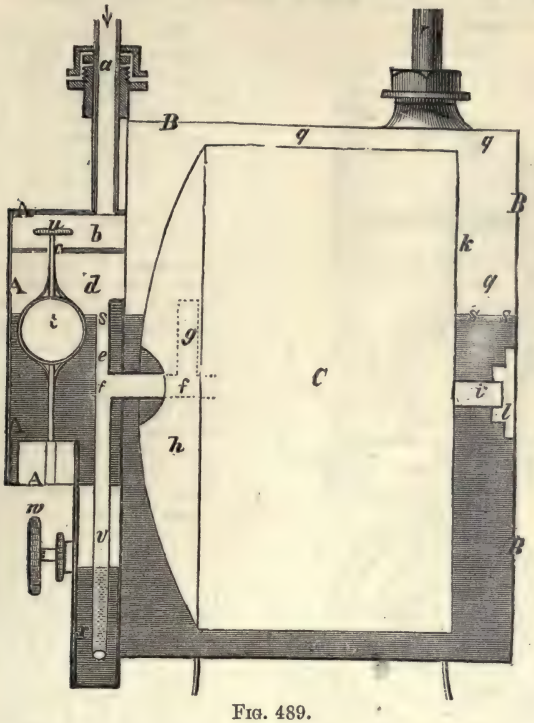


FIG. 489.

space (*d*), containing water at the lower end. From this chamber it passes through the tube (*e*) and through the lateral tube (*f*) into the large cylindrical chamber (B B), and then rises through the tube (*g*) into the front space (*h*) of the drum (C). This drum is closed at the back (*k*), and rests upon an axis (*i*) in the back (*l*) on one side, and at the other on a prolongation of the tube (*f*). The interior surface is not parallel to the axis, but separated by four partitions placed at an incline from one side of the drum to the other, so as to form four separate chambers. The back (*k*) has four slits and thus forms the wings (*m n o p*, fig. 490), situated at right angles with the partitions. The gas by its pressure turns the drum, and as the fissure belonging to each chamber is raised above the water level, the gas escapes into the space (*q*), from which it passes through the tube (*r*) to the burners. By increase of temperature the gas takes up water, and lowers the level of water in the meter. When this takes place, the hollow ball (*t*) sinks, and the plate (*u*) closes the aperture (*c*), so as to shut off the supply of gas, thus indicating that the meter is deficient in water. In order to prevent too much water being put in, so as to fill the tubes (*e f g*), the tube (*e*) has a prolongation (*v*), which dips into a small reservoir (*x*), filled with water up to the level of the screw (*w*). In supplying the meter with water this screw is removed, and when water begins to run out of the hole, the meter has been filled to the proper level. The screw (*w*) is placed at such a height from the bottom of the reservoir (*x*), that the column of water is equal to a pressure of somewhat less than four inches, and thus gas is prevented from escaping through the hole into which the screw (*w*) fits.

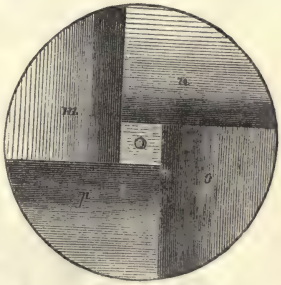
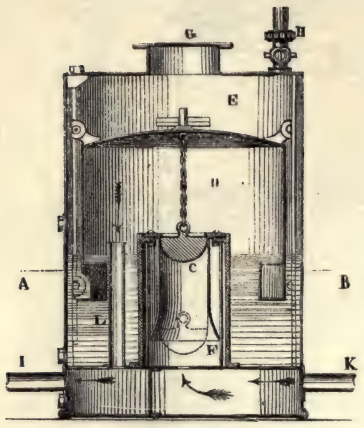


FIG. 490.

The wet meter, when well constructed, measures very accurately, and requires only a slight pressure of gas to work it; but it is liable to derangement by alteration

of temperature. It has therefore to a great extent been superseded by the dry meter, which consists of chambers of definite capacity, and capable of being expanded and contracted. In both cases the quantity of gas passing through the meter is indicated by a clockwork arrangement.

Fig. 491.



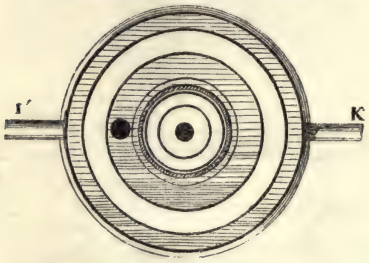


Fig. 492.

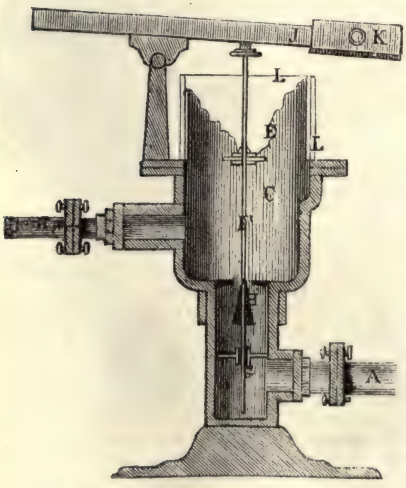


Fig. 493.

The Regulator.—The varying pressure of the gas in the mains depends upon the distance between the gas works and the place where the gas is consumed, and for this reason it is desirable to have regulators connected with the gas supply of each house, in order to maintain a constant pressure. One kind of regulator used for this purpose consists of a small metal bell, so arranged in an outer casing, partially filled with water, that it is raised by increasing pressure of the gas, and entirely closes a conical valve connected with it through which the gas passes; while, on the contrary, with decreasing pressure the bell sinks and opens the valve wider. A regulator of this construction is represented by figs. 491 and 492. At the centre is the valve (C) through which the gas passes attached by a chain to the bell (D), and when it is in the position shown in the drawing, the gas is entirely shut off. When the valve (C) is lowered to the position marked (F) the gas entering through the pipe (K) has free access in the bell (D), out of which it passes through the pipes (L I) to the burners. The pressure of the gas on the bell (D) is regulated by adding or removing cast-iron disks through the opening (G) at the top of the casing (E), within which the bell is fitted. To the top of this casing is fixed a tube (H) which is open to the air and carries at the end a small light metal disk, so that when through any accident the water level in the casing (E) falls too low, or from any other reason gas escapes, it is discharged outside the building. In order to maintain a constant level of liquid in the casing (E), glycerine of 1·143 sp. gr. is used instead of water.

The membrane regulators are preferable to those just described. The construction of one form of this apparatus is represented by fig. 493. The gas enters by the supply pipe (A) and is discharged through the pipe B, after passing through the chamber (C) which is covered at the top with an impervious flexible membrane (E), to the centre of which is attached a rod (F), carrying at one end a conical plug (H) by which the opening of the lower portion of the chamber (C)

can be closed when the membrane is pressed upwards. The tension requisite for effecting this may be regulated by suitably loading the lever (J) to which the upper end of the rod (F) is attached, and for this purpose the lever carries a sliding weight (K) which can be fixed at any part of the lever by means of a screw. The influx of the gas is therefore regulated by adjusting the weight (K), and the gas escapes regularly through the pipe (B) at the pressure required.

The gas consumed in street lamps is not measured, but the quantity burnt within a given time is regulated by a tap, set to allow the gas to pass under a definite pressure at a certain rate. The plan, however, is open to objection, and in some places membrane regulators are fixed to the burners in the manner represented by fig. 494. The gas in passing from the pipes (C and D) to the burner is made to pass through the vessel (A A) fitted with a membrane diaphragm (B B), to the centre of which is attached a rod (*i*) carrying a valve (*r*). The chamber (A A) is divided by the membrane into two parts, so that when the gas passes into it under increased pressure, the membrane is forced upwards into the upper part, and the valve (*r*) being thus raised, it contracts the aperture by which the gas enters from the supply pipe (C) below.

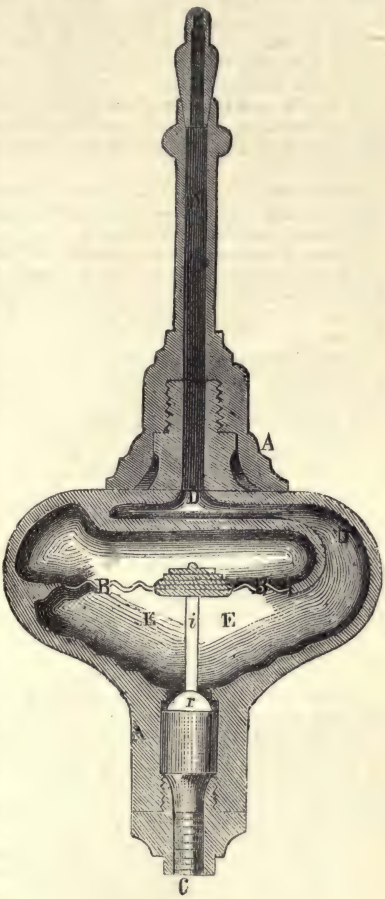


FIG. 494.

A great number of proposed improvements in gas production have been suggested. According to one, the coal is distilled at a much lower temperature than usual, and hence it takes about double the ordinary time. The gas thus produced has a high illuminating power, and a quantity of oily tar is obtained, which is afterwards submitted also to destructive distillation, thus furnishing a further quantity of permanent gas. Practically, the two distillations are conducted simultaneously, the combined result being that a larger yield of gas is obtained, of somewhat higher illuminating power than usual, and, owing to the lower temperature of distillation, containing less sulphur compounds than the gas made by the ordinary process. A special apparatus is required for the distillation of the oil and the additional plant, labour, and fuel required outbalance the favourable results.

Another system aimed at continuous working, and constant and regular removal of the gas produced. It was sought to effect this by introducing the coal into vertical retorts, through a hopper, whence it was carried by the action of a revolving screw down through the length of the retort, reaching the bottom in the form of coke. The resistance offered by the coal to the free revolution of the screw proved an insuperable difficulty in the process, which otherwise promised to yield satisfactory results.

There have also been a number of processes proposed for producing gas suitable for heating purposes from steam, and when further treated for the purposes of illumination. These consist in admitting steam into retorts charged with coal or coke, at a high temperature. The steam is thus decomposed and the hydrogen set free; the oxygen by oxidation of the coke is partly converted into carbonic anhydride, and this by reduction with more red-hot coke becomes partially transformed into carbonic oxide; so that the ultimate result is a non-illuminating gas which consists of hydrogen, carbonic oxide, and carbonic anhydride. To give it illuminating power it is passed through petroleum spirit, and thus saturated with that vapour, or the petroleum is decomposed and the vapour mixed with the gases.

Various other processes have been suggested for making gaseous mixtures of car

bonic oxide and hydrogen, or carbonic oxide alone, for use as fuel, but, with the exception of the method already described at page 589, and the application of the combustible gas from iron smelting furnaces, none of them demand special attention, since none have so far achieved commercial success.

The gas evolved in the distillation of coal, bituminous shale, or other similar materials, for the production of hydrocarbon oil, has generally a high illuminating power, since it contains in large proportion the vapour of the more volatile hydrocarbons produced in the operation. In large works this gas is produced in such quantity, that it is very much in excess of the requirements of lighting the buildings belonging to the works, and it is generally turned to account by burning it under the retorts in which the coal or shale is distilled. Attempts have also been made to convey the gas, thus produced in oil works, through pipes to the neighbouring towns, and there to utilise it for purposes of illumination. It is, however, probable that in this case the illuminating power of the gas would be too much reduced by the condensation of the hydrocarbon vapours if the places to which the gas had to be carried were situated at a very considerable distance from the works where it was produced.

Carburetting Gas.—Various plans of causing any kind of gas to become saturated with coal tar, naphtha, or petroleum vapour, have been proposed with the object of augmenting the illuminating power.

Air saturated with the vapour of volatile hydrocarbons has frequently been proposed as a substitute for coal gas, and if used at once, the mixture serves very well for the purposes of illumination; but when it is attempted to conduct the air gas through any length of pipes, the deposition of the hydrocarbon vapour reduces the quality of the gas.

The extent to which the illuminating power of such gas, prepared with petroleum spirit, depends upon the temperature, is illustrated by the following table, showing the percentage of vapour present in the air gas at different temperatures, when petroleum spirit of 0·650 sp. gr. is used :—

Temperature	Percentage	Temperature	Percentage
10° = 14° F	5·7	15° = 60°	22·0
0° = 32°	10·7	20° = 68°	27·0
10° = 50°	17·5	40° = 104°	39·0

These quantities correspond with the tension of this vapour at the several temperatures, which varies as follows,—

Temperature	Vapour tension	Temperature	Vapour Tension
10° = 14° F	43·5 mm.	15° = 60°	167·0 mm.
0° = 32°	81·0 „	20° = 68°	203·0 „
10° = 50°	132·0 „	40° = 104°	301·0 „

One of the chief difficulties attending the production of this gas consists in obtaining a supply of suitable volatile hydrocarbon. Benzol, or the more volatile portion of gas-tar naphtha, being much in demand for other purposes, bears too high a price to be used for making air gas, or for carburetting. The more volatile portion of petroleum has been therefore chiefly employed, and, as will be seen from the following table, the substances present in oil that does not exceed the specific gravity of 0·660 have a high degree of volatility :—

Specific gravity	Boiling point	Specific gravity	Boiling point
0·600	4°	0·726	118°
0·628	30°	0·741	136°
0·669	68°	0·757	160°
0·699	92°		

This portion of the distillate obtained in refining petroleum or shale oil is unsuited for burning in lamps, and under certain conditions, such as the lighting of country houses and remote villages, its conversion into atmospheric gas may be conveniently carried out; but the supply of a sufficiently volatile portion of petroleum or shale oil is too small to admit of competition with ordinary coal gas. The gas obtained in this way from the volatile petroleum spirit has a density of 1·2 as compared with air, and it consists of about 70 per cent. of atmospheric air, with about 30 per cent. of hydrocarbon vapour. When burnt at the rate of 3½ cubic feet an hour in one of Sugg's argand burners, such gas will give a light equal to about 18 candles.

Fat, resin, and the tarry residue left in distilling petroleum or shale oil sometimes serve as materials for making gas, and although in general they are too costly for ordinary use, they are sometimes preferable to coal, and when the subsidiary products of petroleum or paraffin oil refineries are used, the gas produced requires but little purification.

The retorts used are sometimes horizontal, and arranged in much the same manner as those used in making coal gas. The oil is supplied in a continuous stream, and as it volatilises the vapour passes through a discharge tube into another retort of narrower dimensions, which is kept at a bright red heat, where the oil vapour, coming into contact with the sides of the red-hot retort, is decomposed and converted into gas.

From the hydraulic main the gas passes to a series of vertical condenser pipes, where any remaining suspended particles of oil are separated; then into a washing apparatus and purifiers charged with slacked lime, which extract traces of sulphuretted hydrogen, as well as the carbonic dioxide, before the gas is sent into the gas holder.

In making oil gas the use of an exhauster does not seem desirable, since in this case the prolonged contact of the oil vapour with the sides of the red-hot retorts under a pressure of 3 or 4 inches is requisite for the production of the gas in such a condition that it will burn without producing smoke.

With retorts of the kind above described, about 38 lbs. of paraffin oil can be decomposed per hour, and the yield of gas obtained amounts to about 1000 cubic feet per cwt. The success of the operation depends largely upon the adaptation of the oil supply and the maintenance of the sides of the retorts at a uniform red heat; both conditions being difficult to secure, the result is that the yield of gas is often much below the average, and there is a proportionate increase in the amount of the liquid products.

These difficulties are to a great extent obviated by the use of a retort introduced by Hubner, the general arrangement of which is represented in vertical and horizontal sections by figs. 495 and 496. The body of the retort is formed by a slightly conical cast-iron tube (*a a*) closed above and below, and protected by a fire-clay casing at the lower end. This retort is heated by a flue winding round it and communicating with the furnace at the side. The oil is supplied to the retort through several funnel tubes (*b*) fitted into the upper end of the retort in such a manner, that the oil runs down the heated sides and is there converted into gas, which escapes through the central tube (*e*) into the pipe (*m*), connected with the hydraulic main (*n*). The tubes (*e* and *m*) are furnished with an arrangement (*f*), by which deposits of carbon in the shape of coke or soot can be removed. At the bottom of the retort is a movable mouth piece, which can be removed by loosening the screw (*d*), and the soot or other accumulations can then be drawn out by the rod (*c*). The flue running round the sides of the retort is furnished with several apertures (*k k k k*) by which soot and ashes can be removed.

FIG. 495.

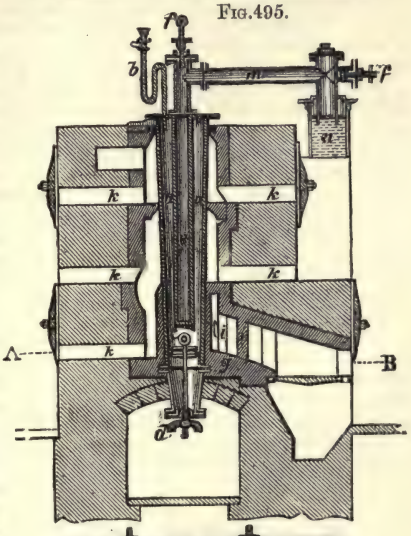


FIG. 496.

The heat produced with this arrangement is very high and uniform, so that from 50 to 80 pounds of oil can be converted into gas hourly, and the yield of gas amounts to 1100 cubic feet per cwt., the illuminating power of which is fully three times as great as that of the ordinary coal gas. The consumption of fuel as well as the labour required are less than with the horizontal retorts, and owing to the uniform temperature obtainable, as well as the small deposition of carbon taking place, the retorts last a long time.

Oil gas has a specific gravity of about 0·7 ranging to 0·6 when the heat applied in decomposing the oil is great, and when it is too low the specific gravity of the gas is sometimes as high as 0·9; its composition is very different from that of coal gas, as shown by the following analyses:—

	Oil gas	Gas from petroleum residues
Olefiant gas and homologues . . .	22·5	17·4
Marsh gas	50·3	58·3
Hydrogen	7·7	24·3
Carbonic oxide	15·5	—
Nitrogen	4·0	—

Gas burners may be constructed on one of two principles, according to the use for which they are intended. If it be required to use the burner for purposes of illumination, its construction differs materially from that adopted when the burner is intended for heating purposes. It has already been explained (p. 23) that flame is merely gas heated to, and maintained by its own combustion at such a temperature, that it emits light as well as heat. But the illuminating power of coal gas is essentially due to the presence in it of dense hydrocarbons such as olefiant gas, and not to the light carburetted hydrogen or the hydrogen which burns with scarcely any light. The production of light in this case has been attributed to the fact that these dense hydrocarbons split up at a high temperature into free carbon, and gases containing less carbon; and although in any case the ultimate products of their combustion are carbonic anhydride and water, yet the evolution of light is to some extent referable to the intensely heated condition of the particles of carbon liberated in the flame, as a result of that decomposition. A mixture of coal gas, with a sufficient quantity of air to effect rapid combustion, burns with a faint blue non-luminous flame, and no carbon is deposited upon a cold plate held in the flame.

It has however been ascertained that the luminosity of flame is not altogether due to the presence of solid particles, and Frankland has shown that marsh gas may be made to give a luminous flame, by heating to redness the gas and the air in which it is burnt. He has also shown that the luminosity of flame is augmented by increase in the density of the air in which gas is burnt, so that the evolution of light attending combustion is a complicated phenomenon influenced by a variety of conditions.

In the combustion of gas for illuminating purposes, the form of the flame depends upon the nature of the aperture from which the gas issues. The batwing burner is formed by a narrow slit across the end of a closed tube, and the flame has the shape of a fan. The fish-tail burner has in the place of the slit two converging round holes inclined towards each other at an angle of 60°. The two jets of gas striking against each other produce a flattened flame.

The Argand burner consists of an annular chamber, the upper surface of which is perforated with a number of holes from which the gas issues in small jets, and is thus brought into sufficient contact with atmospheric air to insure complete combustion. One of the best forms of Argand burner is that introduced by Sugg under the name of the London burner, the construction of which is represented by fig. 497.

In this burner the joint area of the apertures (*f*) through which the gas escapes is much greater than that of the apertures (*g*), by which the gas passes into the annular space (*e*), and thus the pressure with which the gas escapes from the burner is considerably reduced. There is consequently less tendency to mechanical mixture of gas and air at the surfaces of contact, and the flame is very luminous. At the neck (A) of the burner is fixed a conical plug, which fits into the contracted part (*b*) of the tube (C), when the neck of the burner is screwed close down upon the tube (C), but by inserting thin paper washers between this tube and the neck of the burner, the size of the aperture left between the tube (*b*) and the conical plug may be regulated so as to suit the nature of the gas used, and the pressure under which it is supplied to the burner.

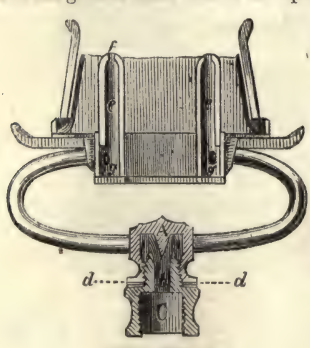


Fig. 497.

When gas is used as a source of heat, it may be burnt either in the form of very small jets, formed by the discharge of the gas through a number of minute apertures in a metal pipe, bent into the form of a ring, or it may be previously mixed with about half its volume of air, and burnt in this state, in what is termed an atmospheric burner. The gas then burns with a blue flame, and does not deposit soot. The several parts of a burner of this kind are represented by

fig. 498. When the piece (*b*) is inserted into the foot (*a*) as shown in the drawing, the gas passes from the supply pipe (*e*) through the channel (*f*), and mixes with air passing in through *g g* into the hollow space (*i i*). By turning the plug (*a*) communication between *e* and *f* may be shut off as far as required.

Another arrangement of atmospheric burner is represented by fig. 499. It consists of a hollow sheet-iron cone (*b*), partially closed at the bottom, and covered at the top with wire gauze. The gas is supplied to the interior of the cone through the tube (*a*), and the mixture of gas and air burns above the surface of the wire gauze, which is sufficiently fine to prevent the flame from being communicated to the gas beneath it.

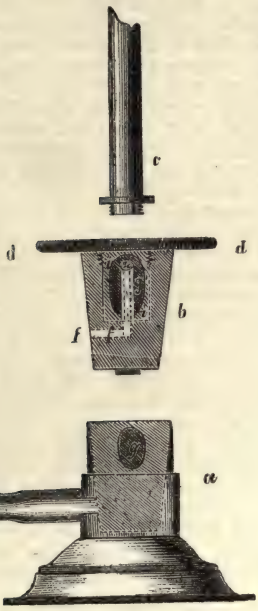


Fig. 498.



Fig. 499.

Owing to the high illuminating power of oil gas, the consumption is not more than one-third or one-fourth as great as when coal gas is used. The apertures of the burners are therefore adjusted, so that under a pressure of about $1\frac{1}{4}$ inch, the quantity of gas burnt per hour is about $\frac{3}{4}$ foot.

When this gas is used mixed with air for producing a heating flame, the ordinary Bunsen burner gives a smoky flame, and acetylene is produced, which causes a bad smell. These inconveniences are prevented by using a burner of the construction represented by fig. 500. The inner tube (*a*) has a screw thread upon which a ring with three arms works up or down, and the conical part of the chimney (*b*) is soldered to the arms of this ring. The lower edge (*c*) of this chimney is ground even so as to fit closely upon the surface of the foot (*d*) of the burner. The first mixture of the gas with air takes place in the tube (*a*), the air being drawn in through the holes (*f*) by the gas flowing through the tube (*e*), and escaping from the aperture (*g*). A further admixture of the gas with air takes place in the tube (*b*), so that by properly adjusting the height of the chimney a clear blue flame is produced.

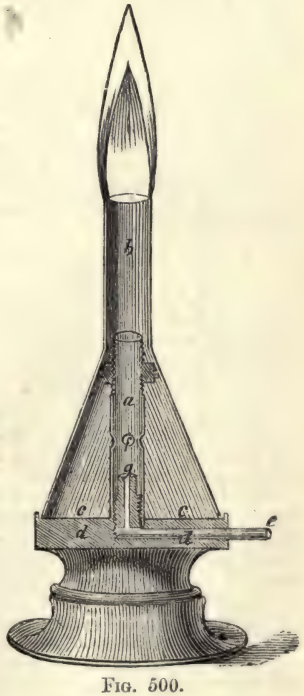


Fig. 500.

Tessie du Motay has introduced a method of burning highly carburetted gas with oxygen, in specially constructed burners of the kind represented by fig. 501, and has succeeded in producing a very much greater luminous effect.

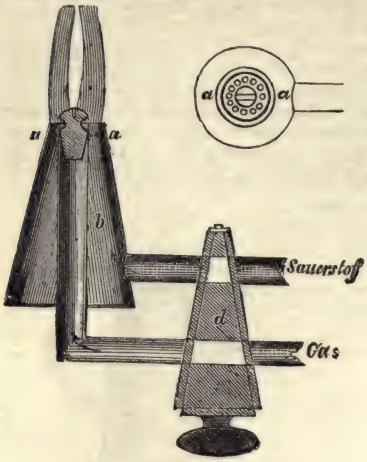


Fig. 501.

The carbonaceous residue or coke left in the retorts in making illuminating gas from coal is an important subsidiary product amounting to from 60 to 75 per cent. by weight of the coal worked. Gas coke is generally much more bulky than the coal from which it is produced, and in some cases it forms a very convenient fuel; its value in this respect depends however upon the amount of ash which it contains. Some kinds of cannel coal which yield a large amount of gas contain so much incombustible material that the coke they yield is not applicable as fuel.

Ammoniacal gas liquor is another important subsidiary product which is largely used for the manufacture of sulphate of ammonia by boiling the liquor with lime in an iron retort and passing the ammonia gas thus liberated into leaden vats containing sulphuric acid (see pp. 49, 52, *et seq.*); as the acid becomes neutralised, and therefore concentrated, the sulphate of ammonium crystallises out and is then baled out and laid upon racks to drain and dry. This manufacture is often conducted on the premises of the gas works, especially in the north of England.

The tar produced in gas making is also a valuable product, and has within the last few years furnished not only a number of products useful in particular manufactures, as for instance, naphtha in caoutchouc working, creasote for preserving wood, and pitch for asphalt paving, etc., but also the raw material of several new branches of industry, especially the benzol naphtha from which aniline dyes are made, and anthracene which is now the source of artificial madder. Carbolic acid also, which is so largely used as a disinfectant and for the production of colours, is obtained chiefly from coal tar.

Gas tar is a thick black liquid having a density from 1·120 to 1·150. It contains a large variety of substances, including ammonia, aniline, picoline, quinoline, pyridine, acetic acid, phenic acid, rosolic and brunolic acids; also benzene, toluene, cumene, cymene, naphthalene, anthracene, chrysene, and pyrene.

When properly distilled it yields a light volatile oil called coal tar naphtha, a heavy oil of high boiling point called dead oil, and a residue of pitch; the relative proportions of these products varying according to the kind of coals from which the tar is obtained.

	Naphtha	Dead oil	Pitch
Common coal tar	3	62	35
Ordinary cannel tar	9	60	31
Boghead cannel tar	15	67	18

The naphtha so obtained is largely used for dissolving caoutchouc.

The dead oil is extensively used as a lubricator for machinery. The black residue left in the retorts on distillation of coal tar, and called *pitch*, is very much used for making certain kinds of asphalt.

The distillation of coal tar is conducted on an extensive scale, as a distinct industry, the operation being performed upon quantities of several hundred gallons at a time in large iron retorts. At first water, ammonia, and some permanent gases previously held in solution by the tar are evolved, after which, as the temperature increases, a light fetid brown oil passes over; this constitutes the light oil, and amounts to about 5 or 10 per cent. of the tar. It is purified by mixing with a little oil of vitriol, which destroys the brown oxidised compounds to which the colour of the crude oil is due, and forms with them a tarry deposit that is easily separated. On rectification the purified oil furnishes coal-tar naphtha, which admits of further purification and fractionation. Dead oil is the heavier yellow oil which comes over after the

naphtha in the distillation of tar, and it generally amounts to about 25 or 30 per cent. of the tar.

Towards the end of the operation, the distillate becomes thicker and contains anthracene. At a still more advanced stage, chrysene and pyrene pass over as orange-coloured vapours, which condense readily on cooling. When the distillation is completed, the pitch remaining in the retorts is run out into a pit underground to cool.

Heavy coal tar oil or dead oil contains carbolic acid, aniline, quinoline, and a mixture of hydrocarbons boiling between 390° and 570°, and containing in solution a quantity of anthracene. Dead oil is largely used for the preservation of railway sleepers; it is also used for feeding common lamps, but mainly for burning into lamp black.

The Examination of Coal Gas.—The gas manufacturer often relies upon specific gravity as an indication of the quality of gas. The photometric method most commonly employed consists in a comparison of the intensity of the light transmitted through a semi-transparent disc of a paper screen, as compared with reflected light striking on an opaque portion of the screen. When the screen is so adjusted that the light reflected and that transmitted are equal, their intensities are to each other in the ratio of the squares of their distance from the disc. The standard ordinarily employed is the light of a spermaceti candle, burning at the rate of 120 grains of spermaceti per hour, and the intensity of the light emitted by a gas flame, consuming in a given time a known quantity of gas, is expressed as being equal to so many candles.

The jet photometer, represented by figs. 502 and 503, is much used in gas works. It is constructed upon the principle that the luminous intensity of different gases is inversely proportionate to the pressure requisite to obtain flames of equal

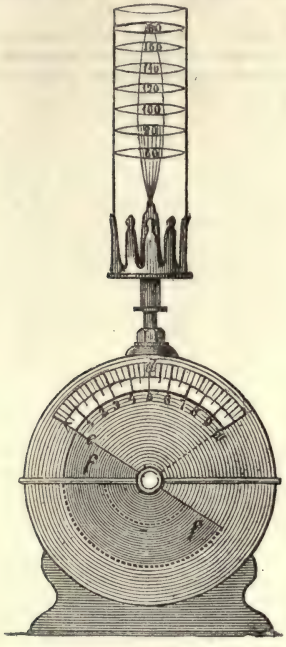


Fig. 502.

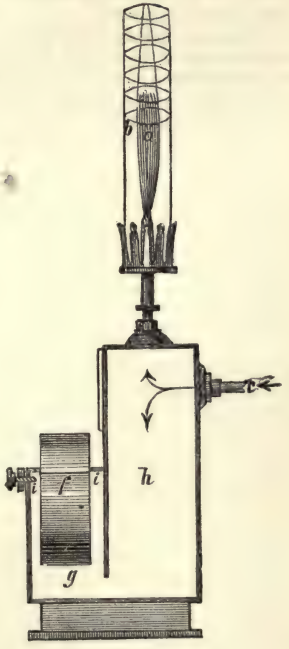


Fig. 503.

height. The flame (*a*) is surrounded by a graduated glass cylinder (*b*), and by means of an adjustment at *e*, the pressure of the gas is measured and registered upon the scale (*d*) by the index (*e*). The index (*e*), is attached to the hollow cylinder (*f*), which is fixed at *i* in a horizontal position, and can be turned on its axis. The weight of this cylinder gives it a specific gravity equal to 0·5. It is immersed up to its point of suspension in water, contained in the vessel (*g*), the bottom of which communicates with the chamber (*h*). Any pressure exerted at the tube (*c*) forces water from the

vessel (*h*) into the vessel (*g*), but it does not rise in this vessel when its volume is less than or only equal to that of the float (*f*). But this float is raised by the water, and thus the pressure is registered by the index on the scale. The instrument therefore shows the quantities of water that must be displaced in proportion to the differences of pressure.

A rough chemical test often used by the practical gas maker consists in introducing into a known volume of coal gas a bubble of chlorine or a trace of bromine, and observing the contraction in volume resulting from the combination of the haloid with the hydrocarbons to which gas principally owes its luminiferous quality.

There are many exact methods of coal gas analysis, one of the most appropriate of which may be briefly described as follows:

A fragment of coke saturated with Nordhausen sulphuric acid is introduced into a measured quantity of the gas over mercury. In the course of a few hours the luminiferous constituents are condensed. The sulphurous anhydride thus formed is removed by means of a pellet of peroxide of manganese; the aqueous vapour and carbonic acid may be then separated by a ball of caustic potash. The difference in the reading of the gas volume then and the original quantity is the expression of the volume of luminiferous hydrocarbons, and as the value of these is ordinarily accepted to stand in relation to the amount of carbon they contain, it may be ascertained by exploding known quantities of the gas both before and after removal of the luminiferous constituents, with excess of oxygen and comparison of the relative amounts of carbonic anhydride produced.

The power of strong sulphuric acid to absorb the luminiferous hydrocarbons was taken advantage of by the Rev. W. R. Bowditch to determine them, by a comparison of the intensity of the red colour which these heavy hydrocarbons impart to woody fibre, moistened with the strong acid. The results obtained by this method are only approximate.

Bisulphide of carbon and sulphuretted hydrogen may be estimated by the use of a simple apparatus devised by Wright, in which a known volume of gas is caused to burn in the presence of excess of air; the amount of sulphuric acid thus produced is an indication of the amount of sulphurous impurity.

ESSENTIAL OIL, CAMPHOR, RESIN, ETC.

A great number of plants contain oily substances which differ from ordinary fat oil in being volatile and having a strong smell, and the characteristic odours of plants or particular parts of plants are in many instances due to their presence. These substances consist either of hydrocarbons, as in the case of turpentine oil, lemon oil, etc.; or of oxygenated compounds, as in the case of winter-green oil, which is methyl salicylate, $C_8H_8O_3$, rue oil, which consists chiefly of euodic aldehyde, $C_{11}H_{22}O$, cinnamon oil and cassia oil, consisting chiefly of cinnamic aldehyde, C_9H_8O, and anise oil, consisting of anethol, $C_{10}H_{12}O$; while other volatile oils consist of mixtures of hydrocarbons with various oxygenated compounds, as in the case of cumin oil, which contains cymene, $C_{10}H_{14}$, together with cumic aldehyde, $C_{10}H_{12}O$, and thyme oil, which contains thymene, $C_{10}H_{16}$, cymene, $C_{10}H_{14}$, and cymophenol, $C_{10}H_{14}O$.

The hydrocarbons occurring naturally in plants have sometimes a composition corresponding with that of cymene, $C_{10}H_{14}$, but more frequently their composition corresponds with that of terpene, $C_{10}H_{16}$, which is the chief constituent of turpentine oil, and since the hydrocarbons contained in some other varieties of essential oil are either isomeric with it, like bergamot oil and neroli oil, or polymeric with it, like copaiba oil and cubeb oil, $C_{20}H_{32}$, the term terpene is applied to them as a generic designation. The chemical constitution of many of these substances is still imperfectly known.

The various kinds of essential or volatile oil occurring in plants often contain solid hydrocarbons, which separate when the oil is exposed to a low temperature, and this solid portion of the oil is called stearoptene, while the liquid portion is called elæoptene.

Two remarkable solid hydrocarbons, known as caoutchouc and gutta percha, which have a composition analogous to some varieties of essential oil, but differ from those substances in not being volatile without decomposition, occur in the milky juice of various species of *Ficus*, *Euphorbia*, *Hevea*, etc., and in the milky juice of *Isonandra gutta*.

The substances known under the name of camphor are in many respects analogous to the various kinds of essential oil, and they not only occur together with terpenes, etc., but are from a chemical point of view closely related to those substances. Although the term camphor is especially applied to the two substances obtained from *Laurus camphora* and *Dryobalanops camphora*, there are several other plants, such as feverfew (*Pyrethrum parthenium*), rosemary, lavender, sage, marjoram, hops, cajeput, peppermint, coriander and patchouli, etc., which contain substances analogous to these more ordinary forms of camphor.

The substances to which the generic name resin is applied often present marked indications of relationship to the several kinds of volatile oil, both in their chemical nature and in their natural association with them. They are generally solid, yellow and translucent bodies of a specific gravity ranging from 0·92 to 1·2; some are hard and friable, but they often occur mixed with volatile oil, forming soft and adhesive or semi-liquid masses, as in the case of pine resin, turpentine, Canada balsam, copaiba balsam, etc. They mostly melt without decomposition, but are not volatile, and at higher temperatures burn with a thick white smoke which is inflammable. When heated in closed vessels most of them yield volatile hydrocarbons; others oxidised volatile products. They are insoluble in water, but soluble in alcohol and ether; those which fail to dissolve in alcohol are usually found to dissolve in ether; they are also dissolved by essential oils, etc. Some few may be obtained in a crystalline form by evaporation of their solutions.

The substances named resins which occur naturally are compounds of carbon, hydrogen and oxygen, and are generally derived by oxidation from hydrocarbons or bodies containing originally less oxygen than themselves. But, as in the case of the

essential oils and the camphors, comparatively little is known of the composition and chemical relations of these substances.

In no case is a resin a simple substance, but it is generally a mixture of several, the various constituent members being referable to as many distinct bodies from which by natural oxidation they are produced.

A considerable number of resins are of an acid character, and in such cases they are competent to produce soaps by combination with alkalies; the soaps thus formed are not insoluble in a solution of salt; nevertheless, ordinary colophony is largely used in soap-making.

The resins are insulators of electricity, and become negatively electric by friction.

The process of extraction of resins from the plants which yield them varies with the circumstances and plant. Many of them are obtained by spontaneous exudation from the growing trees; in other cases incisions are made in the trunk of the tree, and the exuded matter caught in appropriate vessels. In other cases the resins are extracted from plants by means of solvents, such as alcohol, aided by heat.

The best known resins are those produced in the pine and other trees which secrete essential oils. These oils are mixtures of hydrocarbons, often consisting of allotropic modfications and polymers of the body $C_{10}H_{16}$. Thus several varieties of the terpene $C_{10}H_{16}$ may co-exist, together with the polymeric substances $C_{15}H_{24}$ and $C_{20}H_{32}$; from all of these resins are produced by oxidation. So that the resins as they occur naturally are necessarily mixtures and may be very complicated. The act of oxidation may consist in mere addition; or it may be an act of substitution of part of the hydrogen, or part of the carbon may be oxidised as carbonic acid. Any or all of these changes may take place and the nature of the resin produced is determined accordingly.

Besides the resins already mentioned, there is another class termed fossil resins, including amber, asphalt, resins from lignite, and a number of others all of vegetable origin, but scarcely entitled to be considered properly as resins.

In many cases the resin existing in plants is accompanied by and intimately mixed with other substances, such as volatile oil or gum, benzoic acid, etc. These mixed products are known by the names of oleoresins, balsams, gum resins, etc. Thus, for instance, the exudations from some plants are semi-liquid or soft and viscous, and contain a large amount of essential oil; these oleoresins are termed *balsams*, as, for instance, Canada balsam and copaiba balsam, etc., but this term is more correctly applied to materials containing benzoic acid or cinnamic acid together with resin, such as Peru balsam, American liquid storax, Oriental liquid storax, solid storax, tolu balsam, and Mecca balsam, which are among those containing benzoic acid.

In other cases the resin is accompanied by a considerable amount of gum, as in gamboge, olibanum, ammoniacum, and other kinds of gum resin. Sometimes the products belonging to this class also contain essential oil, which gives them an agreeable odour, as for instance, myrrh.

A mixture of volatile oil and resin, constituting the oleoresin known by the name of turpentine, exudes spontaneously from several kinds of pine and fir trees, and is obtained more abundantly by making incisions through the bark of the trees; it is a yellowish white transparent or translucent sticky viscid liquid, having an acid reaction and strong smell. Several kinds of turpentine are distinguished according to the sources from which they are obtained, and they differ in consistency according to the amount of turpentine oil, which varies between 12 and 32 per cent. When the turpentine exudes spontaneously and remains a long time exposed to the air upon the stem of the trees, it hardens and forms what is called pine resin, from which Burgundy pitch is made by melting in water and separating a further portion of the turpentine oil. The resin left as a residue when turpentine is distilled, in order to obtain the volatile oil, is called colophony (see p. 725).

Another kind of oleoresin, called Canada balsam, is obtained from *Abies balsamea*. It is either colourless or pale yellow, has an aromatic odour, is partially soluble in alcohol, and has a right-handed rotation. By distillation with water it yields about 17 per cent. of an aromatic terpene, and a resin of which about one-third is soluble in alcohol, another is soluble in ether, and the remainder is insoluble in both liquids. This variety of turpentine is chiefly employed in cementing optical lenses and microscopic glasses.

Gurgun balsam, an oleoresin obtained from several varieties of East Indian *Dipterocarpus*, resembles capivi balsam in odour and taste, but is heavier. It is readily soluble in alcohol, ether, benzol, and carbon bisulphide. It consists of a crystalline acid, gurgunic acid, $C_{22}H_{34}O_4$, and a hydrocarbon, $C_{20}H_{32}$, that boils at 235° and has a specific gravity of ·9044.

Copaiba balsam is an oleoresin obtained from various species of *Copaifera*. It is a pale yellow thick liquid, of a disagreeable aromatic smell and sharp bitter taste. Its specific gravity varies between 0·91 and 0·99. It is perfectly miscible with absolute

alcohol, bisulphide of carbon, and volatile and fat oils, and readily soluble in ether and acetic ether. It contains a terpene, $C_{20}H_{32}$, of aromatic odour, sp. gr. 0·88 to 0·91, boiling between 245° and 260°, partially crystallisable at 26°, and lævo-rotatory; copaivic acid, a crystallisable substance insoluble in water, soluble in ether and alcohol, $C_{20}H_{30}O_2$; sometimes also oxy-copaivic acid, $C_{20}H_{28}O_3$; and an amorphous neutral resin partly soluble and partly insoluble in alcohol. Some remarkably liquid varieties of Para balsam contain no crystallisable acid, but besides volatile oil only the neutral resin, and the Maracaibo balsam, from Columbia, contains only traces of metacopaivic acid, $C_{22}H_{34}O_4$.

Turpentine oil is the volatile oil obtained by distillation of turpentine, or the oleoresin contained in all parts of the different species of *Pinus*, *Picea*, *Abies*, and *Larix*. According to the particular source from which the oleoresin is obtained, this volatile oil presents variations, chiefly in its physical characters. Four chief varieties of turpentine oil are in this way to be distinguished:—

German turpentine oil, obtained from the turpentine of *Pinus sylvestris*, *Pinus Abies*, or *Picea vulgaris*, *Pinus Picea*, and *Pinus rotundata*.

French turpentine oil, from the turpentine of *Pinus maritima*.

English or American turpentine oil, from the turpentine of *Pinus Taeda* and *Pinus australis*.

Venetian turpentine oil, from the turpentine of *Pinus Larix*.

In addition to these, some scarcely different varieties of volatile oil are obtained by distilling the cones of *Pinus Pumilio*, the fruit of *Pinus Reginæ-Amaliæ*, the needles and branches of *Pinus sylvestris* and *Pinus Abies*.

The crude turpentine oil of commerce contains formic acid, acetic acid, etc., and resinous acids, from which it is separated by re-distillation with water, to which some caustic alkali is added. In a pure state it is a colourless thin liquid, with a peculiar unpleasant smell and burning taste. Its specific gravity varies from 0·86 to 0·87; the boiling point from 152° to 160°. The German, French, and Venetian varieties of oil rotate the plane of polarised light to the left, but in different degrees. The English variety has a right-handed rotation. Turpentine oil is miscible with absolute alcohol, wood spirit, ether, chloroform, benzol, and carbon bisulphide. It dissolves in four times its volume of alcohol of 0·830 sp. gr., and in twelve times its volume of alcohol of 0·860 sp. gr. The varieties of turpentine oil consist chiefly of terpenes or camphenes, together with small proportions of polymeric hydrocarbons. All these substances are susceptible of molecular alteration, especially under the joint influence of heat and pressure, accompanied with alteration of the specific gravity, the boiling point, and especially the rotatory power. When exposed to the air, turpentine oil absorbs oxygen and becomes resinified, while at the same time hydrogen peroxide is formed, together with formic acid, carbonic acid, etc. When water is present, a crystalline hydrated oxide, $C_{10}H_{16}O + H_2O$, is formed, which has a camphoraceous smell and is soluble in water, alcohol, and ether. By contact with dilute nitric acid a crystalline hydrate is formed, having a composition represented by the formula $C_{10}H_{20}O_2 + 2H_2O$, called terpin, and sometimes a liquid hydrate is formed having the formula $C_{10}H_{18}O$. Turpentine oil absorbs dry hydrochloric acid gas with evolution of heat, and when the liquid is kept cold and saturated with the gas, a white crystalline camphoraceous substance is separated after some time, which is insoluble in water, soluble in alcohol and ether, melts at 115°, and has a composition represented by the formula $C_{10}H_{16}HCl$. The liquid portion has the same composition as the crystals, and essentially the same characters. Both the liquid and the solid portions have the rotatory powers of the turpentine from which they have been prepared. Another compound of terpene and hydrochloric acid, $C_{10}H_{16}2HCl$, which is formed by longer continued action of hydrochloric acid gas upon turpentine oil, crystallises in long thin pearly laminæ that melt between 48° and 50°.

Juniper oil, obtained by distilling the unripe berries of *Juniperus communis*, has a sp. gr. of 0·86 to 0·88, distils between 155° and 280°, has a left-handed rotation, is sparingly soluble in alcohol of 0·850 sp. gr., soluble in half its volume of absolute alcohol, and miscible in all proportions with ether. By exposure to the air it is oxidised and deposits a crystalline camphor.

Savin oil, obtained from the leaves, branches, and berries of *Juniperus Sabina*, has a specific gravity of 0·89 to 0·94, boils at 159° to 161°, and dissolves in two parts of alcohol of 0·85 sp. gr.

Cedar oil, obtained from the wood of *Juniperus Virginiana*, is colourless, of a buttery consistence, and consists of cedar camphor, $C_{15}H_{26}O$, and cedrene, $C_{15}H_{24}$.

Sandal wood oil, obtained from *Santalum album*, is a thick yellowish liquid, of powerful odour, having a spec. gr. of 0·963, and distilling between 214° and 255°.

Thuja oil, obtained from the leaves and young shoots of *Thuja occidentalis*, has a camphoraceous odour, and is said to be a mixture of two oxygenated oils

Cubeb oil, obtained by distilling the fruit of *Piper Cubeba*, consists of a light hydrocarbon, boiling at 220°, having a sp. gr. of 0·915, and strong refractive power; and a thick hydrocarbon, having a sp. gr. of 0·937, and boiling at 250°. Both are lævo-rotatory, have a faint aromatic odour and a burning camphoraceous taste. They are miscible in all proportions with ether, benzol, carbon bisulphide, chloroform, and volatile and fat oils, and are soluble in 27 parts of ordinary alcohol, and 18 parts of absolute alcohol. The composition of both is represented by the formula $C_{15}H_{24}$. The oil from old cubebs, when cooled to $-12°$ or $-20°$, deposits a camphor, $C_{15}H_{26}O$.

Pepper oil, obtained from the unripe fruit of *Piper nigrum*; matico oil, from the leaves of *Piper angustifolium*; and the oil of long pepper (*Chavica officinarum*) are sometimes used in medicine.

East Indian grass oil, obtained from *Andropogon Ivarancusa*, is an oxygenated oil. It boils between 107° and 160°, and has a penetrating aromatic odour and a sharp taste.

Citronella oil is an oxygenated oil, obtained from *Andropogon Schœnanthus*. It has a specific gravity of 0·874, and boils at 200°. This is sometimes called geranium oil or palma rosa oil. The volatile oil obtained from *Andropogon Nardus*, in Ceylon, is scarcely to be distinguished from the last mentioned.

Lemon grass oil, obtained from *Andropogon citratus*, is sometimes called verbena oil.

Birch oil, obtained from the leaves of *Betula alba*, consists of a hydrocarbon, boiling at 171°, closely analogous to cymol, and another hydrocarbon, boiling at a higher temperature, which has the peculiar smell of Russian leather.

Hop oil, obtained by distilling the strobiles of *Lupulus humulus* with water, has a sp. gr. of 0·91, boils between 125° and 235°, and consists of a terpene and an oxygenated oil having the formula $C_{10}H_{18}O$.

Hemp oil is obtained by distilling the flowering plant of *Cannabis sativa*.

Cassia oil is obtained from the liber of *Cinnamomum aromaticum*, and probably also from the undeveloped flowers of *Cinnamomum Loureirii*. It is a yellowish or brownish thick liquid, of an agreeable aromatic odour and sweetish burning taste. Its specific gravity is from 1·03 to 1·09; it boils at about 225°. It is highly refractive, but has no rotatory power. It is readily soluble in alcohol, and consists principally of cinnamic aldehyde C_9H_8O, some cinnamic acid, resin ($C_{30}H_{15}O_4$), soluble in alcohol, and a resin ($C_{12}H_5O$) insoluble in alcohol. When long kept it deposits a crystalline stearoptine having a formula $C_{56}H_{29}O_{10}$. This oil is called Chinese, or ordinary cinnamon oil. The Ceylon cinnamon oil, obtained from the bark of *Cinnamomum Zeylanicum*, closely resembles the foregoing. The oil obtained from the flowers of this plant resembles clove oil and pimento oil. It is brown, has a penetrating aromatic odour, biting taste, acid reaction, and sp. gr. 1·053. It contains eugenic acid, benzoic acid, and a hydrocarbon resembling cymol, which has a sp. gr. 0·862, and boils between 160° and 165°. Another oil obtained from the bark of *Persea caryophyllacea*, is pale yellow, heavier than water, and similar in smell and taste to clove oil. Massoy oil, obtained in Java from the bark of *Cinnamomum Kiamis*, is separable by water into a light almost colourless oil of aromatic odour, and a thick heavy oil of less odour: both are readily soluble in alcohol. The oil from the bark of *Cinnamomum Culilawan* is colourless, heavier than water, and smells like cajeput oil and clove oil.

The volatile oil obtained from the fruit of *Laurus nobilis* has a bitter taste, sp. gr. 0·88, and solidifies when cool. It consists of a terpene and eugenic acid.

Nutmeg oil, or mace oil, is obtained from the arillus of the seed kernels of *Myristica moschata*; it consists of a terpene, an oxygenated oil, and a camphor, $C_{16}H_{16}O_5$.

Sassafras oil, obtained from the wood and root bark of *Laurus Sassafras*, is reddish yellow, has a sharp smell, and sp. gr. 1·08. It dissolves in 25 parts of alcohol of sp. gr. 0·850. It consists of a terpene, boiling between 155° and 157°, an oxygenated oil, $C_{10}H_{10}O_2$, boiling between 221° and 233°, and a crystallisable camphor, $C_{10}H_{10}O_2$. It melts between 5° and 17°. Another kind of sassafras oil is obtained in Brazil from *Nectandra Cymbarum*.

Japan camphor oil, said to be obtained from *Laurus Camphora*, has a sp. gr. 0·94, and deposits camphor at $-10°$. The most volatile portion has a composition corresponding to the formula $C_{10}H_{16}O$, and is converted by nitric acid into ordinary camphor.

Borneo camphor oil, occurs, together with a solid camphor, in the stem of *Dryabalanops camphora*, especially in the younger trees. It has a sp. gr. of 0·945. It consists principally of a terpene, some camphor which is deposited on cooling, and a resinous substance.

Valerian oil, obtained from the roots of *Valeriana officinalis*, has a specific

gravity from 0·90 to 0·96; it begins to boil at 200°, and the temperature rises to 400° before the whole distils over. It consists of a mixture of terpene, valerianic acid, and a crystallisable camphor, $C_{12}H_{20}O$, together with some resin.

Chamomile oil, obtained from the flowers of *Matricaria camomilla*, is a dark blue thick liquid, which solidifies at −12° and has a sp. gr. from 0·92 to 0·94. It boils between 240° and 300°. Its composition is represented by the formula $5C_{10}H_{16}.3H_2O$. Its blue colour is due to cœrulin. Roman chamomile oil, obtained from the flowers of *Anthemis nobilis*, is said to be a mixture of angelic acid, $C_5H_8O_2$, angelic anhydride, $C_{10}H_{14}O_3$, together with valerianic acid, or a valerianic ether, and a terpene boiling at 175°.

Wormwood oil, obtained from the flowering plant *Artemisia Absinthium*, has a dark green colour, a burning taste, sp. gr. 0·92 to 0·97, and boils between 180° to 205°; it is dextro-rotatory and very soluble in alcohol. It consists of a hydrocarbon, an oil corresponding to the formula $C_{10}H_{16}O$, and cœrulin. Wormwood oil is used in medicine, and in the preparation of a liqueur.

The volatile oil obtained from *Artemisia Cina* is a brownish yellow thick liquid, of disagreeable smell and burning taste.

Wintergreen oil, obtained from the flowers of *Gaultheria procumbens*, is a mixture of methyl salicylate and a terpene.

Thyme oil, obtained from the flowering heads of *Thymus vulgaris*, has a sp. gr. 0·87 to 0·90, and is lævo-rotatory. It consists of a terpene, thymene, together with cymol and thymol, $C_{10}H_{14}O$.

Peppermint oil, obtained from the plant of *Mentha piperita*, very abundantly in North America, is a mixture of a hydrocarbon and a camphor, menthol, $C_{10}H_{20}O$, which separates at 0° to −8°, plentifully from the American and Japanese oil. It is chiefly used in medicine. Several other species of *Mentha* yield analogous oils.

Lavender oil, obtained from the flowers of *Lavendula vera*, contains several terpene hydrates and a stearoptene. The oil obtained from the leaves and flowers of *Lavendula spica*, called spike oil, has a less agreeable smell, and is more analogous to turpentine.

Rosemary oil, obtained from the flowers and leaves of *Rosmarinus officinalis*, is used in medicine.

Patchouli oil, obtained from *Pogostemon Patchouli*, consists chiefly of a camphor, $C_{13}H_{28}O$, and a hydrocarbon.

Many of the other plants belonging to the *Labiatæ* yield similar kinds of volatile oil.

Rosewood oil, obtained from the root and stem of *Convolvulus scoparius*, consists chiefly of a terpene boiling at 249°.

Anise oil, obtained from *Pimpinella Anisum*, consists of solid and liquid anethol, $C_{10}H_{12}O$. Fennel oil, obtained from *Anethum fœniculum*, has a similar composition.

Cumin oil, obtained from the fruit of *Cuminum Cyminum*, is a mixture of cuminol, $C_{10}H_{12}O$, and cymene, $C_{10}H_{14}$.

Caraway oil, obtained from the fruit of *Carvum Carui*, consists of a terpene boiling at 173°, and carvol, $C_{10}H_{14}O$, boiling above 250°. Many other species of *Umbelliferæ* yield similar kinds of oil.

The volatile oil of meadow sweet consists of salicylic aldehyde, $C_7H_6O_2$, a neutral hydrocarbon, and a crystallisable stearoptene.

Otto of roses, obtained from the flowers of *Rosa centifolia*, *R. damascena*, *R. moschata*, and some other varieties, has a sp. gr. 0·815 to 0·888. It solidifies between 15° and 30°, is sparingly soluble in water, not very readily dissolved by alcohol in the cold, but copiously soluble in hot alcohol. It consists of a liquid oxygenated dextro-rotatory elæoptene, boiling at 210°, and a crystallisable stearoptene, C_8H_{16}, which melts at 35°, boils between 280° and 300°, and sublimes without decomposition.

Lemon oil, obtained from the fruit rind of *Citrus medica* and *C. Limonum*, is limpid, greenish or yellow, has a sp. gr. of 0·84 to 0·86, boils at 160° to 175°, and is dextro-rotatory. It is miscible in all proportions with absolute alcohol, dissolves in 10 parts of alcohol of 0·85 sp. gr., and readily in ether as well as volatile and fat oils. It is a mixture of two terpenes, citrene and citrilene, and a crystallisable camphor, $C_{10}H_{18}O_5$. It is closely analogous to the terpene of turpentine oil in its chemical characters. It is chiefly used in medicine and the manufacture of perfumes. Closely analogous to this are three kinds of orange oil, obtained from the fruit of *Citrus aurantium*, *C. Bigarardia*, and *C. Bigarardia sinensis*; also lime oil, from the fruit rind of *Citrus Limetta*. Bergamot oil, obtained from the fruit rind of *Citrus Bergamia*, is yellowish or pale green, has an agreeable odour, bitter taste and generally acid reaction; it boils between 183° and 195°, has a sp. gr. of 0·85 to 0·88, is dextro-rotatory, miscible in all proportions with absolute alcohol, and readily soluble

in ether and fat oils. It is a mixture of one or two terpenes with a terpene hydrate and a product of oxidation. By keeping the oil deposits a camphor, $C_9H_6O_3$. By contact with water it forms a crystallisable hydrate identical with terpin, and forms a crystallisable compound with hydrochloric acid gas. It is used in medicine, and in the manufacture of perfumery. Neroli oil, or orange flower oil, obtained from the flowers of *Citrus Bigarardia*, has an agreeable odour, a sp. gr. of 0·85 to 0·90, and is dextro-rotatory. It contains a camphene boiling at 173°, an oxygenated oil of higher boiling point, and by keeping it deposits neroli camphor (auradine).

Rue oil, obtained from the leaves and flowers of *Ruta graveolens*, has a sp. gr. of 0·83 or 0·84, solidifies at −1° or −2° in brilliant laminæ, and consists of a hydrocarbon boiling at 200°, and an oxygenated oil of 0·826 sp. gr., boiling between 225° and 226°, probably methyl caprinol or methyl pelargonyl ketone, $C_{11}H_{22}O$.

Cajeput oil, obtained from *Melaleuca minor*, *M. Cajeputi*, and *M. leucadendron*, which are natives of the Molucca and Sunda islands. It has a pale green colour, partly due to the presence of a green resin and partly due to copper. Its specific gravity varies from 0·91 to 0·97. It is readily soluble in alcohol, and consists chiefly of a terpene hydrate, $C_{10}H_{18}O$. It is chiefly used in medicine.

Clove oil, obtained from the flower buds and flower stalks of *Caryophyllus aromaticus*, has a sp. gr. of 1·04 to 1·06, and is lævo-rotatory. It consists of eugenol, $C_{10}H_{12}O_2$, and a hydrocarbon, probably $C_{15}H_{24}$, having a sp. gr. 0·90 to 0·92, and boiling at 142° or 143°. It is used in medicine.

Pimento oil, obtained from the unripe fruit of *Myrtus Pimenta*, has a sp. gr. of 1·03, and is separable by water into a heavy and a light oil. It has the same composition as clove oil, and is separable by caustic potash into eugenol, $C_{10}H_{12}O_2$, and a hydrocarbon, $C_{15}H_{24}$.

Eucalyptus oil, obtained from the flowers of *Eucalyptus globulus*, consists of eucalyptol, $C_{12}H_{20}O$, boiling at 175°, dextro-rotatory, and readily soluble in alcohol. The oil of *Eucalyptus resinifera* contains a hydrocarbon resembling the terpene of turpentine oil. The oil of *E. oleosa* resembles cajeput oil. According to some authorities, eucalyptus oil contains a terpene, cymene, $C_{10}H_{14}$, and an oxygenated oil, $C_{10}H_{12}O$.

Jasmine oil is obtained from the flowers of *Philadelphus coronaria*.

Bitter almond oil, obtained from the fruit kernels of a variety of *Amygdalus communis*, *Amygdalus Persica*, *Prunus Lauro-cerasus*, *P. domestica*, *P. padus*, and from the barks, leaves, and flowers of the last-mentioned plants, as well as from other parts of several plants belonging to the Amygdalaceæ. The volatile oil, consisting of benzoic aldehyde, C_7H_6O, with some hydrocyanic acid, benzoic acid, etc., does not exist in the plants, but is formed by the decomposition of the amygdalin, $C_{20}H_{27}NO_{11}$, which they contain.

The volatile oil of *Cochlearia officinalis* contains sulphur, and is homologous with allyl sulphocyanide, having the formula C_5H_9NS. The oil of *Cochlearia Armoracia* (horse radish) is almost identical with mustard oil, as are also several other oils from various species of *Cruciferæ*.

The oil of *Allium sativum* (garlic) also consists of allyl sulphide, $C_6H_{10}S$, and that of *Allium cepa* (the onion), is essentially identical.

Mustard oil, obtained from the seeds of *Sinapis nigra*, does not exist in them, but is formed by the decomposition of myronic acid, $C_{10}H_{19}NS_2O_{10}$, when the seeds are distilled with water. The oil consists chiefly of sulphocyanide of allyl, C_4H_5NS, sometimes mixed with allyl cyanide.

The substances known under the name of camphor are in many respects analogous to the various kinds of volatile oil; they often occur together with terpenes, and are closely related to the substances of that group. The principal varieties of camphor are camphol or common camphor, $C_{10}H_{16}O$, obtained from *Laurus camphora*, and borneol, $C_{10}H_{18}O$, obtained from *Dryobalanops camphora*. Substances analogous to the former are obtainable from several other plants, such as feverfew (*Pyrethrum parthenium*), rosemary, marjoram, lavender, sage, etc., while others analogous to the latter occur in hops, cajeput, peppermint, coriander, and patchouli.

Laurel camphor is a colourless translucent tough mass, having a crystalline texture, a specific gravity of 0·985, and a peculiar strong odour. It melts at 175°, and distils at 204°, but is slowly volatilized even at the ordinary atmospheric temperature. It is sparingly soluble in water, copiously soluble in alcohol, ether, acetic acid, and hydrocarbons or volatile oils.

Distilled with chloride of zinc, this camphor is converted into cymene, $C_{10}H_{14}$, and water, other products being formed at the same time. When the vapour is passed over heated soda lime, campholic acid, $C_{10}H_{18}O_2$, is formed. By treatment with nitric acid, camphor is oxidised, yielding camphoric acid, $C_{10}H_{16}O_4$, camphoronic acid, $C_9H_{12}O_5$, and oxycamphoronic acid, $C_9H_{12}O_6$. This camphor also forms an oily com-

pound with nitric acid, $2C_{10}H_{16}O.N_2O_5$. This kind of camphor is obtained from Japan and the island of Formosa.

Borneo camphor comes from Borneo, Sumatra, and Labuan. It has a smell somewhat resembling pepper. It melts at 19·8°, and boils at 212°. When heated with nitric acid it is first converted into ordinary camphor, and then into the acids above mentioned. When heated with phosphoric anhydride, it yields water and borneene, $C_{10}H_{16}$, which is probably identical with the terpene contained in ordinary camphor oil.

Borneol is an alcohol, forming with the fatty acids ethers containing the radicle camphyl, $C_{10}H_{17}$.

Menthol, $C_{10}H_{20}O$, is a camphor occurring in peppermint oil. It melts at 36°, boils at 213°, and is lævo-rotatory.

Both laurel camphor and Borneo camphor are dextro-rotatory, but other kinds of camphor are lævo-rotatory.

Colophony is the resin obtained by the distillation of crude turpentine, which often yields as much as 75 or 90 per cent. Two varieties are found in the market, one of which is white and obtained from the *Pinus maritima*; the brown variety is obtained from the *Pinus Abies*.

The brown resin, according to Laurent, consists of two isomeric acids, viz. pinic and sylvic acids, $C_{20}H_{30}O_2$. The pinic acid may be extracted by cold alcohol, and from the residue the sylvic acid is dissolved out by means of hot alcohol, from which it is deposited in colourless prisms or plates that fuse at 127° C. Sylvic acid gives also a crystalline lead salt.

The white resin, or galipot, consists of pimaric acid, which is also isomeric with the acids of the brown resin, and may be obtained in a semi-crystalline state. It is best dissolved by a mixture of 6 parts alcohol and 1 part ether, and may be recrystallised from alcohol; it is freely soluble in ether.

The acids of colophony yield terebic acid $C_7H_{10}O_4$, on oxidation with nitric acid.

When common resin is submitted to distillation in a closed vessel, it yields turpentine $C_{10}H_{16}$, colophene $C_{20}H_{32}$, resinein $C_{20}H_{28}O$, toluol C_7H_8, cumol C_9H_{12}, a substance having a composition corresponding with the formula $C_{16}H_{16}$, naphthalin $C_{10}H_8$, and what is termed metanaphthalin $C_{20}H_{16}$. From this it is seen that common resin does not entirely consist of oxidised compounds, but probably also contains the polymer of turpentine $C_{20}H_{32}$, in a form rendered solid by the true resin.

Copal is obtained from trees of the genera *Hymenæa*, *Trachylobium*, *Voapa*, *Guibourtia*, *Rhus*, *Icica*, *Elæocarpus*, and *Dammara*. It is excreted partly in tears between the bark and wood, and partly collects in large masses about the roots. It has generally a yellowish or brownish, and, less frequently, a reddish colour, is rough and dark at the surface, internally clear and transparent, and is tolerably hard and brittle, the fracture being conchoidal and splintery. It is without odour, and has a specific gravity varying between 1·045 and 1·139; the melting point is between 180° and 340°. Dilute alcohol does not dissolve copal, absolute alcohol dissolves it only sparingly, but the solubility of copal is increased by the addition of camphor or by long-continued melting, or by long exposure of the powdered resin to the air, under which conditions oxidation takes place. In contact with ether the resin becomes gelatinous, and is then soluble in alcohol. Chloroform dissolves it abundantly, benzol slowly; volatile oils and carbon bisulphide dissolve it only partially. The best solvents of copal are the oil obtained by the destructive distillation of caoutchouc and the empyreumatic oil obtained by heating copal to a high temperature. In contact with ammonia solution copal swells up, and when warmed with strong caustic potash it forms a clear solution. The African as well as East Indian varieties of copal consist of five different resins. Copal is chiefly used for making varnishes, and combined with asbestos as a cement for stopping teeth.

Anime, obtained from the West Indian *Hymenæa Courbaril* and sometimes termed copal, has the form of pale yellow translucent fragments, having a sp. gr. 1·028 to 1·03, and a vitreous fracture. It softens in the hand, and smells agreeably aromatic when warmed. It is perfectly soluble in turpentine oil and benzol, and in warm ammonia solution. Cold alcohol dissolves out a volatile and a portion of resin; the residue being crystallisable in boiling alcohol in delicate needles, having the formula $C_{40}H_{33}O$.

Sandarac is the resin that exudes from *Thuja articulata*, a native of Barbary. It forms pale yellow transparent granules, having a specific gravity 1·05, a faint odour, and of somewhat bitter taste. It is easily fusible, brittle, and the surface of the fracture has a vitreous lustre. Sandarac is used for incense and the preparation of varnish.

Dammar. Two kinds of this resin occur in commerce; the East Indian, obtained from *Pinus Dammara*, forms large transparent and colourless or yellowish lumps. It is friable, odourless, and has a resinous taste. Its specific gravity varies from

1·04 to 1·12. At 100° it becomes partially liquid, and it melts at 150°. It is almost entirely soluble in cold ether and in boiling absolute alcohol, and dissolves in fat and volatile oils. It consists of an acid resin, dammarylic acid, $C_{45}H_{37}O_4$, soluble in dilute alcohol; dammarylic anhydride $C_{45}H_{36}O_3$, soluble in absolute alcohol; a solid hydrocarbon, dammaryl, $C_{40}H_{32}$; and a resin, dammaryl hydrate, $4C_{40}H_{32}2HO$(?), insoluble in alcohol and ether.

The Australian dammar resin, or kaurie copal, is obtained from *Dammara australis*, a native of New Zealand. It forms large amber-yellow slightly opalescent lumps, is readily fusible, and perfectly soluble in absolute alcohol. It consists of a crystallisable acid resin, dammaric acid, $C_{40}H_{30}O_7$, and a neutral resin, dammaran, $C_{40}H_{30}O_6$.

Another resin, obtained from *Shorea robusta*, is sometimes mixed with East Indian dammar. These resins are largely used in making varnish.

Elemi, obtained from species of *Icica* and *Amyris*, generally forms yellowish or greenish opaque masses of fatty lustre, which soften between the fingers, are readily fusible, and have a specific gravity of 1·02 to 1·08. It is only partially soluble in cold alcohol, completely soluble in boiling alcohol, and readily soluble in ether and turpentine oil. It consists of about 13 per cent. of a lævo-rotatory camphene, boiling between 166° and 174°, and having a specific gravity of 0·85, a brown amorphous resin, and a crystallisable substance identical with amyrin. Elemi is used chiefly for preparing varnishes and in medicine.

Mastic, obtained from a particular variety of *Pistachio lentiscus*, has the form of tears of a yellowish or greenish colour, covered with a whitish dust, and sometimes having a fissured surface. It is tolerably hard, has a vitreous fracture, and a faint balsamic odour. It softens at 80°, and melts between 105° and 180° with partial decomposition. Its specific gravity is about 1·07. It is readily soluble in benzol and volatile oils; ordinary alcohol dissolves about four-fifths of a resin, the composition of which corresponds to the formula $C_{40}H_{32}O_4$, and a soft resin, masticin, $C_{40}H_{30}O_2$, remains undissolved. It is used in medicine, as incense, for dental cement, etc.

Lac resin, obtained from the branches of *Croton lacciferum*, and probably also from some East Indian species of *Ficus*, *Acacia*, *Zizyphus*, *Aleurites laccifera*, *Croton aromaticus*, *Butea frondosa*, *Ficus religiosa*, and *Zizyphus jugrita*. The female insect, *Coccus lacca*, makes the puncture through which the resin exudes and coats the young shoots, enclosing at the same time the body of the insect. These shoots constitute stick lac. It consists chiefly of a brilliant, brittle, translucent resin, soluble in alcohol and wood spirit, a small proportion of wax, a difficultly soluble resin, and about 10 per cent. of a scarlet pigment known as lac dye. The resin is used for making sealing wax, French polish, and varnish. When the resin is separated from the wood, the pigment is extracted with carbonate of sodium, and the insoluble residue forms seed lac, which, by melting, straining, and pressing, gives shell lac.

Shell lac contains a number of substances, including, according to Unverdorben, oleic and margaric acids. Lac is soluble in a solution of borax, a property which enables it to be distinguished from more common resins with which it is frequently adulterated.

Podophyllin is a resin obtained from *Podophyllum peltatum*. It is soluble in alcohol, partially soluble in ether, and is chiefly used in medicine.

Botany Bay resin, obtained from the stem of *Xanthorrhœa australis*, is reddish-brown, and has a faint benzoic smell. An analogous resin from *Xanthorrhœa hastilis*, has a stronger smell and a bright yellow colour. Both kinds are readily soluble in alcohol and ether, and when treated with water yield gum, cinnamic acid, and benzoic acid. When melted with potash they yield paraoxybenzoic acid, protocatechuic acid, pyrocatechin, and resorcin. They are used for colouring varnishes, and the yellow kind is used in medicine.

Dragon's blood. Three kinds are met with in commerce. East Indian dragon's blood, obtained as an exudation from the cortical scales of the fruit of an East Indian palm, *Calamus Draco*. Canary dragon's blood, obtained as an exudation from incisions in the stem of *Dracæna Draco*. American dragon's blood, obtained in a similar manner from *Pterocarpus Draco*.

The first-named is the most frequently met with. It is reddish-brown, opaque, and bitter, without taste or odour; its specific gravity is 1·196. When melted it gives off an odour of benzoic acid. It is readily soluble in alcohol, less so in ether; also soluble in acetic acid, amylic alcohol, volatile and fat oils. It dissolves in alkaline solutions partially, and acids throw down a yellow precipitate from the solution. The resin purified by solution in alcohol and ether has a composition represented by the formula $C_{40}H_{20}O_8$. When dragon's blood is melted with caustic potash much benzoic acid is obtained, which probably existed ready formed; also protocatechuic acid, paraoxybenzoic acid, and phloroglucin. By dry distillation it yields gaseous

products, and a reddish-black oil containing toluol, styrol and benzoic acid. Dragon's blood is used in medicine, and for colouring varnishes.

Guaiacum.—This resin, obtained from *Guaiacum officinale*, a native of the West Indies, has the form of irregular fragments of a greenish colour, which appear opaque externally, but internally are yellow or reddish-brown. It is hard, very brittle, has a conchoidal, vitreous, splintery fracture, and gives a greyish-white powder. The smell is slight, agreeable, and increased by warming. The taste is at first sweetish bitter, and then sharp and irritating. It melts very readily. Its specific gravity is about 1·2. It is readily and perfectly soluble in alcohol, partially and with difficulty in ether or turpentine oil. It contains about 10 per cent. of guaiaretic acid, $C_{20}H_{26}O_4$; 70 per cent. of guaiaconic acid, $C_{19}H_{20}O_5$; and a small proportion of guaiacic acid, $C_6H_8O_3$, which is soluble in water, and crystallises according to Deville from its alcoholic solution in needles; about 10 per cent. of a neutral resin, $C_{40}H_{20}O_{12}$, insoluble in ether; a crystallisable pigment, guaiacum yellow; some gum, ash constituents, and mechanical admixtures. Guaiacum resin readily melts, and when distilled yields, at a temperature of about 320° C., among other products, the following: a light volatile oil, guaiacene C_5H_8O (b. p. 118° C.), and a substance which sublimes in crystals, pyroguaiacin $C_{19}H_{22}O_3$; also guaiacol $C_7H_8O_2$, a liquid probably homologous with creasote, and boiling at 210° C. This resin is remarkable for its susceptibility to oxidation, and a consequent blue or green colouration. Reducing agents restore the yellow colour. By exposure to the air the change of colour takes place but slowly; most rapidly in violet light; while in red light it becomes yellow. Chlorine and other oxidising agents cause a rapid blue colouration. By dry distillation guaiacum resin yields a thick reddish-brown tar, containing guaiacol, pyroguaiacin, guaiacene, C_5H_8O, and creosol, $C_8H_{10}O_2$. Melted with caustic potash it yields protocatechuic acid. It is chiefly used in medicine.

Myrrh, obtained from *Balsamodendron Myrrha* and *B. Ehrenbergianum*, has the form of irregular yellow, reddish, or reddish-brown fragments. It has a balsamic odour, and pungent bitter taste. Its specific gravity is from 1·12 to 1·28. It contains about 2 per cent. of volatile oil, myrrhol, $C_{10}H_{14}O$, 30 or 40 per cent. of resin soluble in alcohol, which melts at 90° to 95°, is perfectly soluble in ether and acetic acid, but only partially soluble in caustic potash, and 40 or 50 per cent. of gum. When melted with caustic potash it yields protocatechuic acid and pyrocatechin. It is chiefly used in medicine.

Olibanum, obtained in Africa from *Boswellia floribunda* and in Asia from *Boswellia serrata*, has the form of pale yellow, sometimes reddish, translucent or opaque brittle fragments, having a mealy surface and a splintery fracture. Its specific gravity is 1·22. It has a faint balsamic odour and a sharp bitter taste. It melts imperfectly, giving off a pleasant odour. It consists of about 4 or 5 per cent. of a volatile oil, 56 per cent. of a resinous acid, 30 to 36 per cent. of gum, and 6 per cent. of bassorin. It is chiefly used as incense, and to some extent as medicine.

Ammoniacum is obtained from *Dorema Aucheri* and *Ferula tingitana*. The Persian variety forms milk-white or yellowish granules and brownish masses. At the ordinary temperature it is hard and brittle. It softens when moderately heated, but does not thoroughly melt. It has an offensive smell, and a slightly bitter acrid taste. It consists of a resin, $C_{40}C_{25}O_8$, soluble in alcohol, a strong smelling volatile oil, and some gum. African ammoniacum has the form of light brown or yellowish-white masses, and gives off a benzoic odour when warmed.

Galbanum is obtained from *Ferula erubescens* and several other varieties of *Ferula*. It has the form of yellowish or brown granules or masses. It is brittle in the cold, but becomes soft and sticky when warmed. The odour is not disagreeable; the taste is sharp and bitter. It contains a resin, $C_{26}H_{38}O_5$, and a volatile oil isomeric with turpentine oil. By dry distillation the resin yields a thick blue volatile oil, $C_{20}H_{30}O$, and crystals of umbelliferon, $C_6H_4O_2$. When melted with potash it yields resorcin, $C_6H_6O_2$, oxalic acid, and volatile fat acids.

Assafoetida, also obtained from several species of *Ferula*, natives of Persia, occurs as granules, more frequently in large masses. The fresh surface of fracture is white, but soon acquires a reddish violet or yellowish-brown colour. It is readily fusible, has a very disagreeable garlic odour, and a sharp bitter taste. It consists of a sulphuretted volatile oil, $2C_6H_{11}S, C_6H_{10}S$, ferulic acid, $C_{10}H_{10}O_4$, together with resin, gum, inorganic salts, and admixtures of wood and sand. The resin yields, when melted with potash, resorcin, protocatechuic acid, and volatile fat acids.

Sagapenum, obtained from *Ferula szowitziana*, occurs as brownish-yellow or reddish-brown granules and masses. It softens when warmed, but does not melt at a higher temperature. It has a garlic odour, a sharp bitter taste, and is only partially soluble in alcohol. It contains a volatile oil, several kinds of resin, gum, ash constituents, and mechanical admixtures.

Opopanax, obtained from the roots of *Opopanax Chironium*, has the form of granules and lumps of reddish yellow or brown colour and waxy fracture, yielding a yellow powder. The smell is strong and peculiar, somewhat resembling garlic; the taste is bitter. It is only partially soluble in alcohol. It contains a little volatile oil, a resin that melts at 100°, gum, organic and inorganic salts, and mechanical admixtures.

Bdellium, obtained from *Balsamodendron africanum* in Senegambia, and *B. Mukal* in India, has the form of yellow or reddish-brown fragments. It softens between the fingers, smells like myrrh, and tastes bitter. Carana resin, obtained from *Bursera acuminata* in the Antilles, is soluble in alcohol, ether, and alkalies. Gomart resin, obtained from *Bursera gummifera*, in the West Indies and South America, is colourless, crystalline, has an odour resembling turpentine and elemi, and yields about 5 per cent. of volatile oil. Mecca balsam, obtained from *Balsamodendron gileadense*, is a pale yellow thin liquid, readily soluble in alcohol and ether.

Tacamahac, obtained from *Amyris tomentosa*, has the form of yellow or yellowish-brown translucent fragments of sp. gr. 1·46, readily fusible, and soluble in alcohol and potash. It is used as incense.

Icica resin, obtained from species of *Icica* in Cayenne, has the form of yellowish-white fragments or transparent granules of pleasant odour, and is soluble in alcohol and turpentine oil. It consists of two crystallisable resins, brean and icican, and an amorphous resin, colophan, all of which are insoluble in potash.

Euphorbium, obtained from various species of *Euphorbia*, indigenous in Africa and the Canary Islands, has the form of yellowish or brownish-yellow opaque brittle fragments, internally whitish, without smell, but producing irritation to the nose in the form of powder. It is partially soluble in alcohol and in water. It contains about 22 per cent. of a resin, euphorbon, $C_{13}H_{22}O$, soluble in alcohol; 38 per cent. of an amorphous acrid resin, $C_{13}H_{22}O_2$; 18 per cent. of gum, 12 per cent. of malates, and 10 per cent. of inorganic salts. It is used to some extent in medicine.

Ladanum, obtained from *Cistus creticus*, is dark brown, soft, has a sp. gr. 1·86, an agreeable odour and bitter taste. It consists of a resin soluble in alcohol, and another insoluble in alcohol.

Gamboge, obtained chiefly from *Garcinia morella*, a native of Ceylon and Siam, and to some extent from *Garcinia cochinchinensis* and *G. pictoria*, occurring through a greater part of India. It has the form of cylindrical sticks or flat cakes, and has externally a dirty greenish-yellow colour; the fracture is a brilliant brownish-yellow, and the powder bright yellow. In thin fragments it is translucent. It has no smell, but a sharp irritating taste. It softens when warmed without melting, gives off a peculiar odour, and is partly decomposed. It forms an emulsion in water, is partially dissolved by alcohol and more readily by ether, and contains about 72 per cent. of an acid resin, $C_{20}H_{24}O_4$, 23 per cent. of gum, sometimes with admixtures of starch and woody fibre. It is used in medicine, as a water colour, and for colouring varnishes.

Storax. The liquid variety is obtained from the bark of *Liquidambar orientale*. It has a greenish-brown colour, and a smell resembling vanilla and benzoin. It contains styrol, C_8H_8, styracin, $C_{18}H_{16}O_2$, cinnamic acid, benzoic acid, and a resin that is said to be metastyrol. The solid variety is obtained from the same tree, as an exudation that has dried upon the bark in the form of yellowish or brown transparent granules of aromatic odour; it is readily fusible and soluble in alcohol. Both kinds are used in perfumery and medicine.

Benzoin is obtained from *Styrax Benzoin*. It forms roundish reddish-white fragments, internally of a white colour, and reddish-brown masses, or a conglomerate of the two kinds. It has an agreeable odour, and a sweetish pungent taste. When heated it melts and gives off benzoic acid. It is completely soluble in warm alcohol, and partially soluble in ether, and contains three or four kinds of resin, together with benzoic acid, and sometimes cinnamic acid. It is used in medicine, and as incense.

Peru balsam, obtained from *Myroxylon Sonsonatense*, by bruising the bark of the trees and heating it with torches, has the form of a dark brown thick liquid of agreeable odour, sharp irritating taste and acid reaction. Its specific gravity varies from 1·14 to 1·15. It is miscible in all proportions with absolute alcohol; ether leaves a brown smeary residue; hot turpentine oil or almond oil dissolves only about one half. Caustic potash digested with the balsam separates as an upper layer, an oil consisting chiefly of benzyl cinnamate or cinnamein, $C_{16}H_{14}O_2$, benzyl alcohol, C_7H_8O, benzyl benzoate, $C_{14}H_{12}O_2$, and styracin or cinnyl cinnamate, $C_{18}H_{16}O_2$. The alkaline liquor contains cinnamic acid, benzoic acid, a resin soluble in alcohol, and another insoluble in alcohol. Peru balsam is used in medicine, and in making perfumery, chocolate, and for similar purposes. Another kind of Peru balsam, derived from the same source, is obtained by pressing the fruit; it is a thick pale

yellow liquid, with a smell resembling vanilla. When kept for some time it deposits crystals of myroxocarpin, $C_{24}H_{34}O_3$.

Tolu balsam, obtained from *Myroxylon toluiferum*, is, in the fresh state, a yellowish transparent thick liquid. By keeping it becomes reddish-brown and viscid, ultimately drying up to a crystalline brittle resinous mass. It has an agreeable aromatic odour, and a sweetish pungent taste. The solid balsam softens at 30°, and melts between 60° and 65°. It is perfectly soluble in alcohol and chloroform, and partially soluble in ether; it is almost entirely insoluble in ethereal oils and carbon bisulphide. With caustic potash of sp. gr. 1·17 it forms a clear solution, and concentrated sulphuric acid dissolves it with a red colouration. It consists of tolene, $C_{12}H_{18}$, cinnamic acid, benzoic acid, a resin readily soluble in alcohol, and another sparingly soluble in alcohol. It is used in medicine, and in the manufacture of perfumery.

Amber is so well known that its general description is almost unnecessary. Its sp. gr. is slightly greater than water, and it becomes electric on friction. It is found in the beds of brown coal, but is mainly gathered on the coasts of the Baltic, between Königsberg and Memel, after storms. About 13 per cent. of amber dissolves in alcohol and about 10 per cent. in ether. Succinic acid is a product of its dry distillation, and is accompanied by an empyreumatic oil, consisting of mixed hydrocarbons, almost identical in combination with turpentine. According to Schrötter it is that portion of the resin soluble in ether which yields the succinic acid, whereas the oil is supposed to be yielded by the part insoluble both in alcohol and ether.

When amber is boiled with nitric acid, camphor passes over, and succinic acid is formed in the solution.

Applications of Resins.—Amber is mainly used for ornamental purposes; thus it is employed in making bracelets, necklaces, mouthpieces of pipes, etc.

Lac is used in the stiffening of hats, and in the manufacture of the better forms of sealing wax. Löwig gives the following proportions for a good red wax—48 parts of shell lac, 12 of Venetian turpentine, 1 part of balsam of Peru; these are melted together at a gentle heat, and incorporated with 36 parts of vermilion.

Bronzing lacquer is a varnish formed by mixing lac with about half its weight of sandarach, and a little Venice turpentine, and dissolving the whole in 10 or 12 parts of alcohol.

Varnishes.—The principal resins used for making varnishes are copal, anime, mastic, and sandarach. The solubility of copal is increased by powdering and exposing it to the air, when it absorbs oxygen.

Spirit varnishes, which dry rapidly, are made by dissolving the resins in turpentine, wood naphtha, alcohol, or a mixture of two or all of these solvents.

Oil varnishes are made similarly, but a certain amount of drying oil, such as that of linseed or poppy, is incorporated with the varnish. Such varnishes dry more slowly and furnish hard and durable coatings.

Camphor is often used in varnish-making, and of late years a number of other carbon compounds have been used in making patented preparations. Crystal varnish for maps, etc., is made by dissolving Canada balsam in refined oil of turpentine. Varnishes are used, as is well known, for coating the surfaces of wood and metal, and forming hard, glossy crusts which protect the articles from atmospheric influences of a destructive nature.

Caoutchouc.—This substance, which is commonly known by the name of Indian Rubber, occurs in the milky juice of several plants, but only a few, all occurring within the isotherms of 70° F., yield it in quantities sufficient for industrial purposes. It occurs abundantly in various species of *Hevea*, especially in *H. brasiliensis*, Mull (*Siphonia brasiliensis*, Willd.), and *H. guyanensis*, Aubl. (*Siphonia elastic*, Pers.), the juice of which constitutes as much as 0·3 of the entire plant. These plants are operated upon for the extraction of caoutchouc chiefly in Brazil, Guiana, and central America. The product is of good quality, and is generally known as Pará rubber. Other American varieties of caoutchouc are yielded by species of *Castilloa*.

In India, especially in Assam and in Java, caoutchouc is for the greater part obtained from *Ficus elastica* (Artocarpeæ). In the islands of the Indian Archipelago, caoutchouc is obtained from *Urceola elastica* (Apocyneæ), the juice of which is so rich in caoutchouc, that a single specimen of this gigantic tree yields annually fifty or sixty pounds of that substance.

Caoutchouc is further obtained from the following plants: *Camararia latifolia* (Apocyneæ), growing in South America; *Valea gummifera*, growing in Madagascar; species of *Landolphia* in Eastern and Western Africa; *Tabernæmontana utilis*, growing in the equatorial regions of America; and from *Willoughbeia edulis*, and *Melodinus monogynus* (Melodineæ), growing in India.

Caoutchouc consists of carbon and hydrogen, in the proportions represented by the

formula C_4H_7. This formula, however, does not probably represent its molecular constitution, which must be at least C_8H_{14}, in which case caoutchouc might be considered as a higher homologue of acetylene. Caoutchouc in a state of purity is a white, transparent substance, a delicate section of it when placed under the microscope exhibiting a number of small pores, which are, like those of sponge, continuous throughout its mass. The specific gravity of caoutchouc is 0·925. It is a very elastic body, but loses this property when cooled down below 0°, not regaining it until its temperature is raised to about 35° or 40°. On this account, when an expanded piece of caoutchouc is cooled down to a few degrees below 0°, it retains its elongated form, and does not return to its original shape until considerably warmed. Pure caoutchouc is very adhesive, freshly cut surfaces of it adhering well and firmly, when simply pressed together.

Some of the hydrocarbons obtained by the distillation of coal tar cause caoutchouc to swell up, and partially dissolve it. Oil of turpentine that has been dried by distillation over quick lime acts in a similar manner; but better solvents than these substances are found in pure oil of lavender and carbon bisulphide. The fatty oils dissolve only very minute quantities of caoutchouc. Payen has shown that water and alcohol are not entirely without effect upon caoutchouc.

Caoutchouc is hardly attacked by chlorine, and resists almost entirely the action of hydrochloric acid, and all weak acids. In like manner, most gases, and also solutions of potash and soda, are almost without effect upon it. On the other hand, caoutchouc is very strongly attacked by concentrated nitric acid or sulphuric acid, and more especially by a mixture of the two. Caoutchouc yields with sulphuric acid sulphurous acid and a carbonaceous residue; with nitric acid it yields beside a fat-like substance, oxalic acid and camphresinic acid ($C_{10}H_{14}O_7$). Steam exerts a softening effect upon caoutchouc, lessening its tenacity very considerably. Caoutchouc heated alone up to 120° gradually loses its consistency, becoming very sticky; at a temperature of from 145° to 155° it is so sticky at the surface, that it adheres readily to dry solid bodies. At a temperature of about 180°–200° it begins to melt, and apparently passes into another modification, for caoutchouc that has been exposed to such a temperature remains sticky when cold, although its analysis shows it to have the same percentage composition (C_8H_{14}) as before. At a temperature of from 200 to 230°, caoutchouc assumes an oily consistency and becomes darker in colour.

If caoutchouc be ignited, it burns with a bright, somewhat reddish, and very smoky flame, evolving an unpleasant penetrating smell.

When submitted to destructive distillation, caoutchouc yields tar-like products, from which, by means of fractional distillation, hydrocarbons are obtained, belonging probably in part to the olefine series, and partly to the terpene group. The most important of these hydrocarbons are butylene (C_4H_8), caoutchene ($C_{10}H_{16}$), isoprene (C_5H_{10}), and heveene. The boiling points of the products obtained by the fractional distillation of caoutchouc tar are very different, a part boiling at 14°, and others at 33°, 171°, 215°, etc. Most of the substances thus separated from the crude product of distillation are good solvents for caoutchouc.

Among the different sorts of raw caoutchouc imported from various districts of Asia, Africa, and America, the following may be distinguished: 1. Light, opaque caoutchouc, occurring in large irregular pieces; 2. Yellowish, semi-transparent caoutchouc, occurring in irregular plates; 3. A light brown variety, occurring in the form of pear-shaped bottles, spheroidal lumps, or in twisted and woven bands; 4. Another brown variety, having an irregular cubical shape and rounded corners and edges.

The light colour and opacity of the first kind depend upon its containing a considerable quantity of water, more or less of which every sort of caoutchouc is liable to contain. The brown colour of most of those sorts of raw caoutchouc occurring in the market is due to admixture, pure caoutchouc, as already observed, being colourless.

If caoutchouc be allowed to remain thirty days in water, its pores get filled with water, a consequence of which is that its weight increases from 18·7 to 26·4 per cent., and its volume about 15 or 16 per cent., while on the other hand its tenacity and adhesiveness decrease.

When thick pieces of caoutchouc have become permeated with water, it is extremely difficult to deprive them again of the entire quantity absorbed, as upon drying the caoutchouc, the water escapes first of all from the surface pores, and these then contracting, prevent the escape of water from the interior of the pieces. On this account, the lighter coloured kinds of caoutchouc, containing absorbed water, are of less value, not only because their weight is thus increased, but also because, in order to expel such water by drying, the pieces have to be cut into thin bands.

When treated with boiling water, many kinds of caoutchouc yield a resinous substance.

Absolute alcohol, especially when heated, penetrates caoutchouc quicker than

water, producing, like the latter substance, a lighter coloration of the caoutchouc. Caoutchouc that has been steeped in absolute alcohol for a space of eight days, the alcohol being heated at intervals, becomes more opaque and adhesive, its volume increases about 9·4 per cent., and its weight about 18 per cent., while the alcohol dissolves out of it about 2 per cent. of a yellow fatty oil. After the evaporation of the alcohol absorbed the caoutchouc is not so tenacious as it was before, while on the other hand it is more transparent and adhesive.

Ether, benzol, oil of turpentine, carbon bisulphide, etc., or mixtures of them, penetrate caoutchouc very quickly, cause it to swell up and appear to dissolve it completely. The solution is however only a partial one, nearly the whole of the solution remaining in the expanded insoluble portion, as in a sponge, the entire piece retaining the original shape, only much enlarged. The non-soluble portion contains the brown colouring matter, while the soluble portion, upon evaporation of the solvent, exhibits a slightly tinged, soft, and flexible mass, which is but slightly tenacious or elastic.

Caoutchouc repeatedly treated with anhydrous ether gives up to this solvent 66 per cent. of an almost colourless substance, and 34 per cent. of residue remains having a colour varying from yellow to brown.

Pure anhydrous oil of turpentine dissolves out from caoutchouc 49 per cent., leaving 51 per cent. of residue. The soluble portion is left, upon evaporation of the solvent, as a light brown mass, the insoluble residue being darker coloured. But if the oil of turpentine contain a mere trace of any resinous body, the soluble as well as the insoluble portion assumes a sticky consistency, dries difficultly, and decomposes readily when exposed to the air.

Caoutchouc that has been exposed for a long time to the action of the sun's rays in a warm atmosphere undergoes a peculiar change which has been termed solarisation, its surface becoming less elastic; anhydrous benzol then extracts from it a substance which, upon the evaporation of the solvent, does not possess the elasticity and tenacity of ordinary caoutchouc, but is friable and brittle.

That this decomposition is owing to a process of oxidation may be seen from the following results of an analysis by Spiller of some solarised caoutchouc:—

Carbon	63·00
Hydrogen	8·50
Oxygen	27·50

Pure caoutchouc, as already observed, contains only traces of oxygen. Gutta percha, under the same conditions, undergoes a similar decomposition.

A very peculiar behaviour is exhibited by caoutchouc in respect to sulphur. When these two substances are melted together, caoutchouc absorbs indefinite quantities of sulphur, but when only a comparatively small quantity has been absorbed, the caoutchouc does not present any alteration of its chief physical properties. This product of the action of sulphur upon caoutchouc is termed vulcanised caoutchouc. When caoutchouc has been made to absorb much sulphur, a solid mass is obtained having a hornlike consistency, and called vulcanite.

Caoutchouc is prepared by inspissating the milky juice of the plants yielding it. The juice, not containing it in solution but suspended in it in a very fine state of division, is generally obtained by cutting the bark of the tree so as to rupture the laticiferous vessels, situated principally in the middle layer of bark, or mesophlœum; care should be always taken not to cut sufficiently deep to injure the cambium layer underneath. The cuts are sometimes made in a spiral form, and sometimes as two series of diagonal incisions running into a common channel cut perpendicularly in the trunk. The juice flows into hollows made at the bottom of the tree. The plants do not yield any juice from the trunk during the flowering period, and the tapping operation should not be performed at that time, nor during the wet season, as the juice then contains a larger proportion of water.

The inspissation has to be performed as rapidly as possible, as the juice easily decomposes and becomes sour, especially in the sun. It is sometimes heated over a fire in clay moulds of various forms. A thick mass of caoutchouc being difficult to dry throughout, only small quantities of juice are treated at a time, to which other portions are added successively, lumps of caoutchouc of any desired thickness being thus obtained. The caoutchouc thus dried together with the clay mould is then placed in water, and the softened clay removed; the product thus obtained is known as raw caoutchouc. In other places the juice is often dried with the smoke of a fire in wooden moulds. In the East Indies it is often dried directly in the air in the hollows at the foot of the trees, protected however from direct sunlight.

Anthoine exhibited at Paris in 1855 caoutchouc separated from the juice by the addition of from 2 to 3 per cent. of spirits of wine. The juice thus treated forms two layers, the upper containing the coagulated caoutchouc, which is removed

and thrown upon a piece of linen stretched upon a frame and lying upon sand; the water then filters into the sand and the caoutchouc is dried in the air. A method somewhat similar to the above is employed in St. Salvador, where the fresh juice is mixed with double its volume of water, and allowed to stand twenty-four hours, when, as in the former case, the caoutchouc forms a layer upon the surface of the water. It is washed several times with water, a small quantity of a solution of alum is added, the caoutchouc separated from the water, and dried. In Nicaragua the coagulation of the juice is effected by the addition of the juice of other plants, one of which has been identified as the *Ipomœa bona-nox*.

Caoutchouc, as already observed, occurs in the market in various forms. A very excellent and pure caoutchouc is that imported from Para (Brazil). It is more valuable than other sorts of caoutchouc, and occurs in the form of pear or bullet shaped bottles, having an exterior diameter of about 5 inches, with sides 2 inches thick, or in the form of round disks, 2 inches thick and 8 inches in diameter, or in the form of plates of the same thickness as the disks.

From Java a brown, very elastic kind of caoutchouc is imported, containing however 10, and sometimes 15 per cent. of foreign admixtures. It occurs in the market in the form of cubical-shaped pieces, from 8 to 10 inches in length, which are formed from plates and bands pressed together.

From Valparaiso (Chili) is imported a darker brown sort of caoutchouc, more elastic than the above, and occurring in thick plates.

The caoutchouc imported from Gabon, in Africa, is of a lighter colour, containing water; it is elastic, but more easily decomposed under the action of light and air than that from Valparaiso. It occurs in broad thick ribands.

From Carthagena (New Granada) caoutchouc is imported in the form of brown, fibrous plates, that are tolerably elastic.

The caoutchouc imported from Buenos-Ayres occurs in thick shapeless pieces, white, and containing water.

From Assam (Asia) caoutchouc is imported in irregular blocks, formed of light and dark kinds kneaded together; it often contains foreign substances, as well as a considerable amount of water; it has good elastic properties, but decomposes gradually on exposure to light and air.

Vizagapatam exports a peculiar kind of caoutchouc, which at present has not found much employment. It occurs in the market in the form of hard, unelastic plates, from $\frac{1}{8}$ to $\frac{1}{4}$ inch thick, which become soft and sticky when heated, resuming their original properties upon cooling.

A great quantity of caoutchouc comes to Europe which has got damaged by fermentation, produced by the watery sap enclosed in it.

Caoutchouc has been known and used in South America and India for a very long time. It found its way into Europe at the beginning of the 18th century, having been introduced by M. de la Condamine, who sent specimens of the substance from Peru to Paris, and at the same time made known the fact that it was obtained by drying the milky juice of certain plants. In 1751 MM. Fresnau and Macquer discovered the caoutchouc tree in Cayenne, and shortly afterwards communicated details as to the method of obtaining caoutchouc.

For a long time the only employment made of caoutchouc was for rubbing out from paper the marks of a lead pencil, and hence its name Indian rubber; in 1790, it was used for making gum balls, elastic bands, valve springs, and for rendering coarse tissues impervious; in 1791 M. Grassart made tubes of it. In 1820 M. Nadler succeeded in cutting caoutchouc into threads fine enough for preparing various objects, and especially elastic tissues. A few years later Mr. Mackintosh perfected the manufacture of caoutchouc tissues, rendered them impervious to water by employing a mixture of oil of turpentine and caoutchouc, and made waterproof mantles of this article. It was not, however, until the discovery of the method of vulcanising caoutchouc that caoutchouc found the extensive employment it now enjoys.

The first patent for a method of sulphurating caoutchouc was taken out in 1839, by Mr. Goodyear in the United States, but he gave at that time neither the amount of sulphur nor the temperature necessary for its combination. He made, however, in 1844 a more complete report upon the properties and advantages of sulphurated caoutchouc, and the process being so akin to the attributes of the Vulcan of Mythology, was termed by Mr. Brockedon, vulcanisation, which name it has retained.

In the same year Mr. Hancock produced vulcanised caoutchouc by using a bath of molten sulphur. In 1846 Mr. Parkes described the process of vulcanising caoutchouc by means of a mixture of carbon bisulphide and sulphur chloride.

Caoutchouc juice is not simply an emulsion of caoutchouc in water, as it contains other constituents.

Faraday analysed a specimen of caoutchouc juice imported from America, which upon drying yielded 45 per cent. of caoutchouc. He found it to contain—

Caoutchouc	37·70 per cent.
Vegetable albumin	1·90 „ „
A bitter nitrogenous substance, soluble in alcohol and in water	7·13 „ „
A substance insoluble in alcohol	2·90 „ „
Water	56·47 „ „

Adriani gives the following results of an analysis of the sap of *Ficus elastica* obtained upon making an incision in a terminal bud:—

Caoutchouc	9·57 per cent.
A substance soluble in alcohol, but insoluble in ether	1·58 „ „
An organic acid in combination with magnesium	0·36 „ „
A substance insoluble in water	2·18 „ „
Salts of sodium and potassium	traces
Water	82·30 „ „

It follows from the above analyses that the caoutchouc of commerce is not pure caoutchouc, for when prepared by simply drying the sap it contains, besides caoutchouc, all the other constituents of the sap, such as albumin, resinous substances, salts, etc. When caoutchouc is prepared by separating it from the sap and washing with water it is certainly purer, being then free from substances soluble in water, but it still contains substances insoluble in that menstruum.

It has been attempted to import caoutchouc juice in the fresh state. It retains its quality without becoming acid, when mixed with a small percentage of ammonia water (5 to 7 per cent.), and kept in vessels hermetically closed.

Vulcanisation of Caoutchouc.—Before the discovery of the process of vulcanising caoutchouc had nothing like the extensive employment which it now enjoys, for its property of becoming soft at a temperature of from 30° to 50°, and of becoming very hard at temperatures below 0°, rendered its employment in either very hot or very cold climates impossible.

These inconvenient properties of caoutchouc are got rid of by combining it with sulphur; when thus combined it retains its elasticity and flexibility at temperatures varying from 20° to 180°. Its adhesive property is however entirely lost, and on this account it is not possible to combine pieces of vulcanised caoutchouc by simple pressure.

If a plate of caoutchouc, from $\frac{1}{12}$ to $\frac{1}{6}$ inch thick, be plunged into melted sulphur having a temperature of from 115° to 120°, and kept in it for two or three hours, the caoutchouc absorbs from 15 to 20 per cent. of its weight of sulphur, without its physical properties becoming materially altered. It is as elastic as before, and pieces of it can be united by the aid of pressure. Just as little change takes place when caoutchouc is either brought into contact with sulphur dissolved in carbon bisulphide, or kneaded with sulphur at a temperature of from 25° to 40°, but its porosity is diminished by its pores having become filled with sulphur.

If caoutchouc, thus penetrated with sulphur, be heated up to 132° or 140°, an important change takes place in a few minutes; long exposure to this high temperature deprives it of its flexibility; it becomes hard and unelastic. It is then capable of taking up enough sulphur to constitute 48 per cent. of the entire vulcanised product; this would remain even after treatment with potash or soda, which are unable to dissolve out the sulphur thus chemically combined.

By the action of sulphur upon caoutchouc, some sulphuretted hydrogen is produced and the melted sulphur is capable of absorbing a quantity equal to its own volume. This gives rise to the following curious phenomenon. If a piece of caoutchouc be dipped in a sulphur bath, and the bath then allowed to cool, at the moment of crystallisation of the sulphur, the sulphuretted hydrogen that had been retained in the liquid sulphur escapes, and being then mechanically imprisoned between the crystals of sulphur, causes a rising of the whole mass.

In a compound of caoutchouc and sulphur containing only 1 or 2 per cent. of the latter, the relation between the carbon and hydrogen of the caoutchouc is not perceptibly altered. Caoutchouc, when sufficiently vulcanised, does not contain more than 1 or 2 per cent. of sulphur in a state of chemical combination; the rest, which often amounts to from 5 to 15 per cent., may be extracted by treatment with caustic potash or soda. Sulphur which has been simply mechanically retained in vulcanised caoutchouc, if not removed by the agency of solutions of soda or potash, escapes in course of time through the pores of the caoutchouc in the form of a fine powder. This

efflorescence also occurs when caoutchouc plates, into which an excess of sulphur has been kneaded, are allowed to remain at rest for a long time.

Carbon bisulphide, benzol, and oil of turpentine, also cause vulcanised caoutchouc to swell up, its volume increasing ninefold upon long contact with these liquids. Sulphur not chemically combined is then dissolved, and can be extracted by this means.

The several sorts of caoutchouc differ considerably in their capacity for absorbing water. Payen conducted comparative experiments with: 1. Non-vulcanised, or fresh caoutchouc; 2. With vulcanised caoutchouc; 3. With desulphurised caoutchouc; and found that the first absorbed from 20 to 26 per cent. of water, the second 4·2 per cent., and the third 6·4 per cent.

Further, a bottle with sides $\frac{1}{12}$ inch thick, filled with water under pressure in such a manner that its diameter becomes doubled, loses by evaporation in twenty-four hours and at a temperature of 16° C., for every square yard of surface, about 280 grains of water when made of common non-vulcanised caoutchouc, and only about 50 grains when made of vulcanised caoutchouc. Balloons of this kind filled with air under a similar pressure, and at the same temperature, do not suffer any noticeable loss.

The Vulcanising Process.—There are various methods now in use for vulcanising caoutchouc. The first English patent was taken out by Mr. Hancock. It consists in dipping the caoutchouc into sulphur melted in an iron vessel, at a temperature of from 115° to 120°, and allowing it to remain until it has absorbed equally throughout its mass about 15 per cent. of sulphur. After the caoutchouc has been taken out of the sulphur and got cool, its exterior adherent coating of sulphur is scratched off, and it is then heated to between 132° and 140°; an operation technically termed burning the caoutchouc, as it is when this temperature has been attained that the sulphur combines chemically with the caoutchouc, and produces in it that marvellous change which distinguishes vulcanised caoutchouc from common caoutchouc.

According to Mr. Goodyear's method, powdered sulphur is kneaded with caoutchouc, in a machine constructed for the purpose, until it has taken up from 10 to 15 per cent. of sulphur; it is then heated up to and kept at a temperature of from 132° to 140°, until it has chemically combined with about 2 per cent. of sulphur.

Mr. Parkes, of Birmingham, introduced the use of carbon bisulphide in the sulphuration of caoutchouc. According to his process, pieces of caoutchouc are dipped, for a length of time varying with their thickness, into a mixture of 100 parts of carbon bisulphide, and $2\frac{1}{2}$ parts of sulphur chloride. The liquid penetrates the caoutchouc, causing it to swell up, a part of its hydrogen being replaced by sulphur derived from the sulphur chloride. When taken out, the pieces are rapidly dried in a current of dry air. In the case of thick pieces, it is necessary to dip them often, so as to insure their thorough penetration by the liquid.

This method of Parkes was improved by Gérard, who suggested dipping the pieces of impregnated caoutchouc into lukewarm water immediately after their removal from the bath, so as to avoid the reaction of the sulphur chloride upon the surface of the caoutchouc during the drying; the sulphur chloride becoming decomposed upon contact with the water.

Another method is also due to Mr. Parkes, according to which the caoutchouc is kneaded together in a kneading machine, with from 10 to 13 per cent. of a solid mixture of sulphur and sulphur chloride, until a complete mixture has taken place.

Gérard introduced a method of vulcanising caoutchouc, which consists in heating the caoutchouc for three or four hours with a solution of calcium pentasulphide, having a specific gravity of from 1·200 to 1·245, at a temperature of 143° C., and under a pressure of four atmospheres. The liquid penetrates pieces of caoutchouc, which are not too thick, completely, affording them the necessary quantity of sulphur with which they combine. After removal from the bath, they only require to be washed with water and dried.

Gérard's 'alkaline caoutchouc,' which is said to resist most reagents well, is prepared in the following way. The caoutchouc (100 parts) cut into ribands is covered with a mixture consisting of 6 parts of powdered sulphur, and from 6 to 10 parts of powdered calcium hydrate, and kneaded together with this powder by means of hollow cylinders, heated internally by steam to 40° or 50°, until a combination of the powder with the caoutchouc has taken place. The next operation is to heat the caoutchouc thus treated, for one and a half or three hours in hermetically closed vessels, either in steam or water according to the thickness of the pieces. This causes a combination of sulphur with the caoutchouc, a part of the sulphur and lime being dissolved out as calcium sulphide and hyposulphite. This method yields a vulcanised rubber more sulphuretted internally than externally, so that its surface is less friable and brittle.

Propositions were made in the first instance by Mr. Hancock, and afterwards by others, to replace sulphur by other substances for vulcanising purposes. Of the substances proposed may be mentioned artificially prepared antimonous sulphide, mixtures of zinc white and sulphur, of pipe clay and sulphur, lead hyposulphite and sulphide, and lead sulphide and bismuth sulphide.

Decomposition of Vulcanised Caoutchouc.—If vulcanised rubber be heated for any length of time to 130° C. in contact with metals, a double reaction takes place; on the one side free sulphur combines with the caoutchouc rendering it too strongly sulphurated, and at the same time a sulphide of the metal is produced.

Vulcanised caoutchouc when exposed to light and air also undergoes oxidation, which renders it brittle. According to Gérard, this objectionable property may be overcome by mixing the caoutchouc before vulcanisation with some anhydrous coal tar.

Vulcanised caoutchouc does not swell up so much in benzol as non-vulcanised caoutchouc. Ether or carbon bisulphide dissolve out from it about 4 or 5 per cent. of caoutchouc, as well as the chemically uncombined sulphur. Vulcanised caoutchouc, when immersed for two months in a mixture consisting of 10 parts of carbon bisulphide and 4 parts of absolute alcohol, yields to this menstruum 25 per cent. of caoutchouc and 10 per cent. of sulphur, 65 per cent. remaining behind. That vulcanised caoutchouc is less easily penetrated by liquids than ordinary caoutchouc has already been mentioned.

Desulphuration of Vulcanised Caoutchouc.—An excess of sulphur in vulcanised rubber may act very injuriously; methods have therefore been devised for getting rid of the chemically uncombined sulphur. This is generally effected by boiling the vulcanised caoutchouc in a solution of caustic soda or potash, until the excess of sulphur is dissolved.

Vulcanised caoutchouc, thus desulphurated, is quite as durable as that which has not been so treated; it has however this inconvenience, that tubes made from it become after a time stiff, and when packed together for any length of time, stick to one another. They soon regain perfectly their former ductility and elasticity, when stretched strongly a few times.

To prepare Threads of Raw Caoutchouc.—The most regularly shaped and least vesicular bottles of Para caoutchouc are softened in hot water, cut in two, and pressed into disks between strong metal plates at a temperature of 100°, and they retain the discoid form upon cooling. These disks are then fastened to a rotatory apparatus with their centre opposite a circular knife in rapid motion, upon contact with which the entire disk is cut up into a band having a spiral form. Adhesion of the caoutchouc to the knife is prevented by keeping the knife constantly wet with water. The bands are next passed through circular slitters, by which they are cut into long threads. Such threads are of the most elastic and durable kind, but possess the inconvenient property of becoming hard at a temperature a little below 0°, and soft a little above 30°. For weaving purposes they are cooled below 0° C., and the fabric afterwards rendered elastic by raising its temperature to 45°.

Purification of Raw Caoutchouc.—Caoutchouc, as it is found in the market, generally contains a number of impurities, consisting partly of mechanically enclosed woody particles, leaves, etc., and partly of normal constituents of the caoutchouc sap; it has therefore in most cases to undergo a process of purification before it can be made use of for industrial purposes. For this purpose it is first softened in warm water, then cut by means of a circular knife into pieces of ½ inch to 2 inches in thickness, and finally squeezed between a couple of rollers over which a continuous gentle stream of water is permitted to flow. These rollers are either equal in diameter (about 16 inches), and one rotates more slowly than the other, or they have unequal diameters and similar rates of rotation. The pieces of caoutchouc are thus pressed and torn into the form of broad shreds, so that they offer the largest possible amount of surface for being washed in a solution, consisting of warm dilute caustic soda into which they are next plunged. In some places a rag machine, similar to that used in paper manufactories, is employed, instead of the mill used for tearing the pieces of caoutchouc. In this case, however, the caoutchouc must have been already torn to shreds. The raw caoutchouc imported from Brazil is purer than that from India, and does not need this energetic cleansing process; it only requiring a single laceration and simple washing with water.

Reunion of washed Caoutchouc is effected by kneading the pieces in an apparatus termed the wolf (figs. 504 and 505). This consists of a strong cylinder of sheet iron divided into two parts, the lower part (BB) being fixed, while the upper part (CC) moves on an hinge (O), and can be opened by aid of a handle (M). A strong iron roller (A) furnished with teeth rotates in the interior of the cylinder, making from 60

to 100 revolutions per minute. The other half of the cylinder is surrounded below with an iron jacket (E E), so as to allow of its being heated by steam. About 30

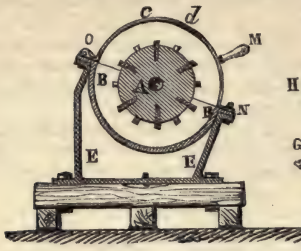


Fig. 504.

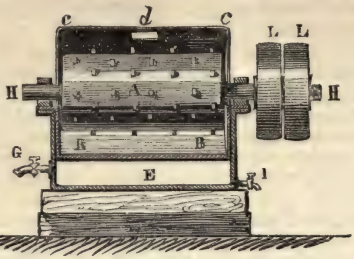


Fig. 505.

lbs. of well washed and dried caoutchouc shreds are thrown into the cylinder B B, the cylinder is then firmly closed, and the roller A set in motion. The pieces of caoutchouc are kneaded and squeezed together in the comparatively narrow space between the interior sides of the cylinder and the roller, until they become united into a single lump.

For the first ten or fifteen minutes in all seasons, and for the whole time during the winter, the union of the pieces is facilitated by heating the cylinder to 45°C. by letting steam into E E through the cock (G). The extent of conglomeration is observed by means of an aperture at *d*.

The caoutchouc lump, being under considerable pressure in the cylinder, alters in shape very much when taken out. After a lapse of about ten minutes it assumes the form depicted in figs. 506 and 507, having a diameter of about 7 or 8 inches, and being about 16 inches in length, while the surface of the roller is only about 2½ inches apart from the interior of the sides of the cylinder, and the ends of the cylinder only about 14 inches apart from each other.

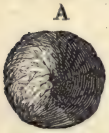


Fig. 506.

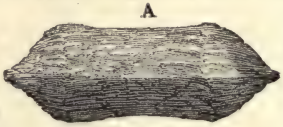


Fig. 507.

The force required for the revolution of the roller is as much as 5 or 6 horse power, as the caoutchouc mass, rendered sticky by the heat produced by friction, etc., adheres fast to the sides of the cylinder and has to be torn away by the roller; the roller making from 80 to 100 revolutions in a minute, and the caoutchouc lump only 3 or 4. This apparatus has undergone several improvements. Guibal employed a fluted roller in the place of the toothed one; Aubert and Gérard line the bottom of the cylinder also with quadrilateral teeth.

Rolling mills have been much used recently instead of the wolf, being more simple and not requiring the application of so much force.

Mr. Goodyear's rolling mill consists of two strong hollow rollers of wrought iron, placed either against or over each other, and set within $\frac{1}{6}$ or $\frac{1}{4}$ inch of one another. The rollers are heated by steam, and the dried and washed pieces of caoutchouc are pressed between them until they appear homogeneous throughout. Sometimes one of the rollers is fluted parallel to its axis, and rotates 1½ times more frequently than the other. The rollers generally lie perpendicularly one above the other, and have a length of 2½ feet and a diameter of 13 inches, being capable of working up at one operation upwards of 40 lbs. of caoutchouc.

When regularly formed blocks are desired, the raw shapeless pieces are cut into disks, and being placed one above the other are squeezed together under a powerful hydraulic press at a temperature of 45°, either alone or in an iron mould. A block thus formed, being allowed after cooling to remain six or eight days under pressure, retains the shape given to it when removed. The blocks are then stored up for use in a cellar.

Plates of any desired thickness may be cut from blocks by fixing the block with caoutchouc cement upon a movable slide placed in a horizontal position, and pressing against it a thin very sharp knife oscillating 800 or 900 times in a minute. The thickness of the plates is regulated by a screw arrangement, which raises the level of the slide holding the block. Adhesion between the knife and the caoutchouc is prevented by a stream of water which keeps the knife continually wet. By this means

plates may be cut of any thickness from $\frac{1}{75}$ of an inch upwards. These serve for the manufacture of light balloons, tubing, elastic garters, and various chemical and chirurgical instruments and utensils. All such objects, however, require vulcanising, for reasons already given.

Guibal prepares cylindrical blocks directly from the irregular lumps (figs. 506 and 507) as they are turned out from the kneading apparatus. A block is pressed with great force while still warm into a strong cylindrically-shaped iron mould, placed vertically, by means of a ram fitting into the mould, and moved by an hydraulic press; it is allowed to remain 24 hours or longer under pressure.

These cylindrical blocks are generally cut into long bands, the width of which corresponds to the height of the cylinder, by means of a circular knife pressed against it in a direction parallel to the axis of the cylinder.

Bands are easily united, the ends being laid over one another, and either squeezed together in a press or welded together with a hammer upon an anvil like pieces of iron. In this operation it is necessary to work in a room having a temperature of 25°, the caoutchouc having been previously brought to this temperature. Should the bands or plates of caoutchouc have cooled to below 0°, they must be heated to 40° or 44° in order to give them their former elasticity and adhesive properties. The various objects manufactured from these caoutchouc sheets, such as tubes, overshoes, balloons, bottles, etc., have then to be vulcanised in one of the ways already described.

Threads.—For preparing threads from purified rubber, plates $\frac{3}{4}$ or 1 inch thick are either punched or cut into disks 6 or 8 inches in diameter. These disks are then cut into spiral bands, and finally into threads, by being passed through circular slitters. Another method is to cut the disks direct from cylindrical blocks, and then into threads.

Another method differing considerably from either of the above, consists in stretching a piece of India rubber tubing over a roller having a screw arrangement, and placed against a sharp knife in such a way that upon moving the roller in the direction of the screw line, the caoutchouc tube is cut into one long thread, the breadth of which throughout is the same as the width of the grooves in the screw.

A machine constructed by M. Gérard is capable of cutting from 150 to 250 threads in a single operation. Bands of the best Para caoutchouc are drawn out between warm rollers and kneaded up with 6 per cent. of sulphur. Upon coming from the rollers, the bands are strewn on either side with powdered talc, and wound round other rollers together with strips of linen. The length of an individual band is about 66 yards, its width about 26 inches, its thickness varying from $\frac{1}{50}$ to $\frac{1}{8}$ inch, according to the thickness of the threads to be made from it. The rolled up bands, together with the rollers, are placed in a strong vertical iron cylinder, and heated for a couple of hours by means of superheated steam to a temperature of 140°. In order that the bands may have perfectly parallel sides, their edges are cut when cool, and the bands are then divided lengthways by three parallel incisions into four parts. The ribbons thus formed are then drawn over a roller composed of 150 or 250 sharpened steel disks, having a diameter of $2\frac{3}{4}$ inches, and a thickness of $\frac{1}{250}$ inch, and separated from one another by disks of brass $2\frac{1}{3}$ inch in diameter, and $\frac{1}{50}$ to $\frac{1}{8}$ inch thick, according to the thickness of the threads to be produced. These disks are attached to an axle, and pressed firmly together by means of a screw adjustment. The whole forms a roller, the entire surface of which is covered by circular knives projecting about $\frac{1}{5}$ inch. This is set in rapid motion (about 1,500 revolutions in a minute), and the prepared caoutchouc ribbon is drawn under it by means of a smaller roller placed parallel to the first, which makes only 8 or 10 revolutions in a minute, and being pressed at the same time against the cutting roller by means of a caoutchouc band, is thereby cut into threads. Adhesion of the threads is prevented as in other instances, by a stream of water kept flowing over them. The cutter is at first slightly raised, and then lowered on the ribbon, in such a manner that an end piece remains uncut. As the cut ribbon leaves the cutter, the individual incisions are seized by a comb, the teeth of which correspond with the circular knives of the roller. The incisions are so fine, that ribbons cut in this manner, upon coming from the cutter, look just like uncut ones. The slightest touch, however, is sufficient to show the division in 150 to 200 threads. In order to render the surface of the threads more pliable, they are wound into skeins upon reels, drawn from thence through a heated solution of potash, then washed with water and afterwards dried in the air. Finally, to prevent them sticking together, they are wound round vertically placed frames, furnished with copper teeth, and then either packed at once, or worked in the loom.

According to Payen, this machine yields from ten to fifteen times as great a quantity of caoutchouc thread as the ordinary machines employed.

Round Caoutchouc Threads.—The manufacture of round threads of caoutchouc is also due to MM. Aubert and Gérard; it consists in pressing caoutchouc that has been rendered plastic by some solvent, through round holes, and carefully drying the thread. Caoutchouc, cut into small pieces, is placed in hermetically closed tin boxes, with an equal weight of 5 per cent. alcohol, and allowed to remain some time. The caoutchouc swells up without dissolving, and forms, after standing twelve hours, a pasty mass. As it generally contains mechanical impurities which would be disadvantageous for the next operation, the pasty mass is forced through a sieve in which the impurities remain behind. The caoutchouc is then passed into a strong iron cylinder, the bottom of which is furnished with round holes having tin points, which give it the required form. The caoutchouc paste is pressed through these holes by a piston that exactly fits into the cylinder. The threads upon issuing from the holes are very soft, and require careful drying. To effect this, they are wound over an endless cloth of cotton velvet, passing over two rollers set at a distance of 13 feet from each other. The threads are wound from this cloth on to an endless wire sieve, likewise turning upon two rollers set apart at a distance of about 40 inches, and are here dusted with powdered talc to prevent adhesion. Finally, the threads are drawn over five endless linen bands, each of which passes over two rollers set apart at a distance of 52 feet. The threads, upon leaving the linen bands, are completely dry, the whole process of drying occupying only ten minutes.

The thickness of the threads is of course dependent upon the size of the holes at the bottom of the cylinder through which the caoutchouc is pressed, but, as the thickness diminishes considerably during the drying, threads passed through a hole of $\frac{1}{25}$ inch in diameter, have when dry a diameter of only $\frac{1}{36}$ inch.

The packing of the threads is performed by passing them directly from the linen bands through a funnel into a tin box, revolving on its axis, by which means they get laid together in the box in regular convolutions.

Very thin threads of caoutchouc are prepared by stretching thicker ones until these have attained the required thinness, when they are submitted for some time to a temperature of 115°; after cooling the threads retain the elongated form, but are not further altered by the operation.

Solid Balls of Caoutchouc.—These are generally made from the caoutchouc blocks (figs. 506 and 507), as they are turned out of the wolf. The blocks are pressed with some force against rollers, the surface of which is furnished with saw blades running parallel to the axis of the roller, so that the points project beyond the rolier, like the rasps of the roller employed in sugar manufactories. These rollers, which make from 500 to 600 revolutions in a minute, tear the caoutchouc into shreds, and at the same time heat it sufficiently to cause it to form a soft sticky mass, which is then made with the hand into rough sorts of balls, that are afterwards pressed in moulds. These moulds consist of two movable halves, fitting over one another, and the soft caoutchouc getting into the groove between them, the balls exhibit a distinct ring when cool. This ring can be got rid of by changing the position of the balls in the moulds after the first pressing, and squeezing them again. The balls are cooled down in the moulds for about twelve hours, before being taken out. They are rendered again elastic by being heated to 50° in a heated room or in hot water.

A cloth-like covering is sometimes given to these balls by smearing them with caoutchouc cement, and rolling them in fine wool. The wool sticks to their surface, forming, after the balls have been dried in a warm room, a very durable covering.

When a permanent elasticity is to be attained by vulcanising the caoutchouc, about 6 or 8 per cent. of sulphur is added to the caoutchouc in the wolf, and the balls made from such vulcanised rubber are brought, while still in the moulds, into a cylinder heated to 140°.

Rolled Caoutchouc Plates.—These are made by rolling thick and large pieces of caoutchouc previously heated to 40° or 50°, then rolled out between warmed rollers which are brought gradually nearer together, the operation being repeated until the desired thickness is attained. The rollers are heated to 80° or 100°, either by bars of red-hot iron let into them, or preferably by steam.

As the sheets of caoutchouc leave the rolling machine in a very warm and half sticky condition, they are passed through cold water rendered slightly alkaline, or covered with talc powder before being folded up.

Coloured Caoutchouc Plates are prepared by mixing up with the caoutchouc some non-transparent colouring powder. White plates are obtained by the addition of zinc white, red ones by adding cinnabar, yellow or orange by adding different ochres, blue ones by adding ultramarine, and black ones by adding ivory black or lamp black, etc.

Caoutchouc Foot Rugs have recently come much into vogue. They generally have a raised pattern, and those having a dimension of about 6 feet by 3 are made from a

single thick caoutchouc plate in a single pressing. The caoutchouc plate, in which sulphur has been kneaded, is pressed strongly between two hollow iron plates upon which some design is engraved, and heated by steam conducted through the hollow iron plates first of all for a short time up to 115°, and finally to 145° C. so as to vulcanise the caoutchouc. As it is easy to conduct several pressings together upon a long strip, Aubert and Gérard prepare pieces of caoutchouc carpet for galleries, etc., upwards of 100 yards in length.

A mixture suitable for the purpose has the following composition:—

Caoutchouc	50 parts
Teazed linen	15 „
Zinc oxide	25 „
Sulphur	4 „
Slaked lime	5 „
Chalk	6 „

M. Guibal prepares network door mats from the following mixture:—

Caoutchouc	40 parts
Chippings of vulcanised rubber	10 „
Other caoutchouc chippings	5 „
Litharge	35 „
Chalk	8 „
Sulphur	2 „

India Rubber Tubes are generally prepared from strips of sulphurated but unburnt caoutchouc, the width of which corresponds to the diameter of the tube. The caoutchouc strip is folded together, and the sides clipped off in the manner represented in section by fig. 508. The cut surface A forms with the lower surface on one side an angle of 45°, and on the other an angle of 135°, so that both surfaces fit exactly together when laid over one another. The operation of laying over is assisted by a mandrel made of iron tube or wire, as shown by fig. 509, and the surfaces are united by strong pressure. Another way consists in winding the caoutchouc slip round the mandrel and uniting the edges.

Fig. 508.



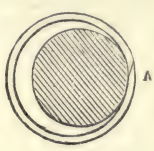


Fig. 509.

The burning (i.e. the completion of the vulcanisation) is the next process, which is performed by binding the tubes and mandrels round with linen strips, and heating them in iron cylinders by means of steam to a temperature of 132° or 140° for between 1½ and 2 hours. The mandrel, the thickness of which must correspond to the bore of the tube, is drawn out after the burning. Should it adhere to the tube at any part, it may be liberated by means of a little cold water.

Tubes that are required to resist strong internal pressure are prepared in the following way. A linen band previously dipped in caoutchouc varnish is wound in a spiral manner round a tube of sulphurated but unburnt caoutchouc; the whole is then surrounded by a second caoutchouc tube, and burnt in the manner above described. Tubes of still greater durability are made by using iron wire instead of linen.

India rubber tubes may be also prepared by using a press like that described in the manufacture of round threads, mandrels being fixed in the moulding holes.

A mixture recommended by Payen for the preparation of India rubber tubes has the following composition:—

Caoutchouc	59 parts
Zinc oxide	35 „
Sulphur	5 „
Lime	1 „

Waterproof fabrics, and very thin Plates of Caoutchouc.—Two distinct methods are followed in the manufacture of waterproof fabrics:

(1) Thin caoutchouc plates are pressed into or upon the stuff;

(2) The caoutchouc is spread upon the stuff in the form of varnish.

In order to prepare waterproof materials from thin plates of caoutchouc, the plates in a non-vulcanised, still adhesive state are placed between two pieces of cloth and then passed several times between heated rollers. By this method, waterproof fabrics are obtained which are rather heavy, but are free from the unpleasant smell which clings to other waterproof stuffs when solvents are used. The method was invented by Mr. Macintosh, who employed it in the preparation of the first waterproof fabrics.

Lighter waterproof stuffs are obtained by rolling together a single piece of cloth

with a single piece of caoutchouc. The fabric obtained is thus covered on one side only with caoutchouc.

The second method for preparing waterproof fabrics, which consists in covering the cloth with caoutchouc varnish, has been recently much employed. Strips of purified caoutchouc are thoroughly dried by leaving them in a drying room for twenty-four hours, and are then softened by immersion for from twenty-four to forty-eight hours in three times their weight of rectified oil of turpentine in wooden boxes lined with sheet iron, each box holding about 110 gallons. The expanded caoutchouc mass is distributed in eight metal cylinders with perforated bottoms, so as to form a layer of $2\frac{1}{3}$ inches in height in each cylinder. These eight cylinders are then placed in a column apparatus, similar to that used in distilleries, closed hermetically with a lid, the whole being fitted over a still filled with rectified oil of turpentine. The turpentine is made to boil; its vapour, passing through the perforated bottoms of the cylinders, raises the temperature of the caoutchouc to about 150°, and permeates it more completely than is the case in a simple process of kneading. The turpentine vapour passes out through a tube at the top of the apparatus into a serpentine condenser, the condensed product being again used as rectified oil of turpentine.

At the end of two hours the operation is stopped, the cylinders taken out of the column apparatus, and the caoutchouc thrown into a kind of vermicelli press furnished with 3 or 4 fine metallic wire nets attached to perforated sheet iron. A piston fitting accurately into the press is then set in motion by means of a screw, and the caoutchouc mass is pressed by it through the wire sieves, which retain mechanical impurities. The soft caoutchouc mass is then strongly rubbed and kneaded between rollers; and, when a colour is desired, the colouring material to the amount of $\frac{1}{2}$ per cent. is thrown in. Blue is obtained by adding ultramarine, yellow by the addition of orpiment, white is produced by zinc white, red by powdered cinnabar, and black by lamp black, etc. When vulcanisation of the caoutchouc is required, from 3 to 4 per cent. of sulphur is added. The apparatus represented by fig. 512, p. 744, may be used for these operations. Should the caoutchouc paste not be soft enough, from $\frac{1}{2}$ to 4 parts of oil of turpentine are added to 1 part of caoutchouc.

The oil of turpentine employed in the preparation of this caoutchouc paste should be pure rectified oil, raw non-rectified turpentine containing always considerable quantities of resinous substance.

M. Guibal employs benzol in the place of oil of turpentine, the articles manufactured from caoutchouc paste prepared with benzol having the advantage that they are not injured by the action of the air, like those manufactured from varnish or paste prepared with oil of turpentine. The cause of the latter being affected by the air seems to be owing to a decomposition, caused by a small quantity of oil of turpentine retained by the caoutchouc.

The caoutchouc paste or varnish is spread upon the cloth in a well-ventilated room protected as far as possible from dust, the cloth being placed on an endless band revolving round two horizontal cylinders, set apart at a distance of about 30 yards. Across this band, and perpendicular to it, is fixed a wooden scraper edged with iron, and having adjusting screws by which the thickness of the caoutchouc layer can be regulated.

As soon as the cloth is in movement, the caoutchouc paste is laid upon it with a trowel in front of the scraper, under which it passes in a more or less thin layer, according as the scraper is set. The speed is about 11 yards a minute, so that a web 64 yards long makes a single revolution every seven minutes. An interval of two hours is allowed between the application of each layer of paste, so as to insure the evaporation of the greater part of the oil of turpentine; a coating of 14 layers would therefore require from twenty-eight to thirty hours. This inconvenient delay, caused by the time required for the evaporation of the oil of turpentine, has been avoided by Messrs. Guibal and Cuminge, who have constructed an apparatus in which the web is passed over heated boxes; evaporation of the oil of turpentine or benzol is by this means so accelerated that the whole operation may be completed in two hours. In order to recover the turpentine thus evaporated, Messrs. Guibal and Cuminge have constructed a condensing apparatus just over the spot where the chief quantity of oil of turpentine or benzol evaporates. It consists of a couple of pieces of sheet metal laid together to form a kind of roof, and kept cold on the outside by a current of water.

If the caoutchouc has been previously kneaded with sulphur with the object of eventual vulcanisation, it is now heated for an hour to 132° or 140° in an iron cylinder with double sides, between which steam is passed. For the most part linen stuffs only are vulcanised, stuffs of silk or wool being very apt to crinkle and pucker at the high temperature required for vulcanisation.

Double textures, or textures which consist of a layer of caoutchouc between two layers of web, may be also prepared by the aid of this apparatus. For this purpose two

lengths of coated web are laid together with the caoutchouc sides against one another, and pressed firmly together into one piece by passing them between rollers.

Instead of the scraper arrangement for regulating the thickness of the caoutchouc layers, two rollers are sometimes employed, through which the coated webs are passed. The upper roller is stationary, the distance between it and the lower one being regulated either by adjustment screws or a lever arrangement. The lower roller revolves in the direction of the cloth.

Various recipes have been given for preparing the caoutchouc paste.

Guibal recommends the following mixture as forming a cheap and durable caoutchouc paste, void of disagreeable smell:—

Purified caoutchouc	33 parts
Powdered litharge	50 „
Chalk	10 „
Lamp black	2 „
Sulphur	5 „
	100 „
Benzol	100

Payen recommends the following mixture:—

Caoutchouc	30 parts
Powdered litharge	50 „
Chalk	10 „
Lamp black	2 „
Sulphur	4–5 „

A method of softening and partly dissolving caoutchouc with carbon bisulphide in the cold, and kneading the mass to a homogeneous paste or dough, is employed in preparing the caoutchouc for the double textures already alluded to.

Stuffs of the kind have this advantage, that carbon bisulphide volatilises more quickly than oil of turpentine. Indeed it sometimes evaporates too quickly, and in order to prevent a too rapid volatilisation a small quantity of benzol is added.

When carbon bisulphide is employed, the process must be conducted in a well-ventilated room, so as to prevent the workmen suffering from the stupefying and poisonous vapours of that substance.

Mr. Norris suggested a direct application of raw caoutchouc sap to webs to be coated with caoutchouc. Mr. Goodyear recommends the addition of oil of tar, and more sulphur than is usual. M. Chevalier has recommended boiling caoutchouc that has been previously softened by oil of turpentine, with a mixture of linseed oil and litharge, etc. An interesting patent for preparing caoutchouc paste was taken out by Mr. Fry, which consists in submitting to distillation a mixture of two parts of rectified oil of turpentine with from three to four parts of caoutchouc, using the distillate as a solvent for caoutchouc.

The apparatus for the manufacture of waterproof fabrics above described may be advantageously used in the preparation of very thin sheets of caoutchouc, and the caoutchouc used may be either pure or after it has been treated with colouring, litharge, sulphur, etc.

In this case, the linen cloth which runs over the two rollers receives a coating, consisting of equal parts of treacle and gelatine. This gelatine covering is on the one hand dry enough to prevent substances adhering to it, and on the other hand, owing to the hygroscopic properties of treacle, moist enough to retain its flexibility for a long time. The caoutchouc paste is spread upon the gelatine coating and the cloth passed under the scraper; 40 very thin coatings being applied for the preparation of a sheet $\frac{1}{25}$ inch thick. The spreading of each layer occupies about 10 minutes, the drying itself an hour, so that a sheet of 40 coatings requires 40 hours for its preparation. The sheets are easily removed from the gelatine coating, are then covered with finely-powdered talc, and wound up on rollers.

These very thin sheets of caoutchouc are well adapted for the production of a number of objects, which, when the caoutchouc has been previously kneaded up with sulphur, may be vulcanised by simply heating them.

In order to give the sheets a smooth surface, they are boiled for about an hour with a solution of caustic soda or potash; they are rendered still smoother by drawing them through a solution of potassium hypochlorite heated to 60° (Javelle water).

Hollow Balls are prepared from caoutchouc plates $\frac{1}{6}$ to $\frac{1}{4}$ inch in thickness, and occur in the market in sizes varying from 2 to 5 inches in diameter. The plates themselves are prepared either by cutting up blocks of caoutchouc with the oscillating knife, or are rolled out; the caoutchouc mass is generally previously mixed with 5 or

6 per cent. of sulphur, so as to admit of eventual vulcanisation. The plates are cut into spherical segments upon a model, and in such a way that the cut surfaces have an oblique direction, which renders their union more easy. Four such segments are taken for a single ball, and their edges united either by simply pressing them together with the hand, or sometimes with the aid of a cement consisting of caoutchouc, sulphur, carbon bisulphide, and benzol, care being taken that as much air as possible remains in the ball. The balls are then placed in spherical moulds, something like those employed in bullet-casting, and heated in iron cylinders to over 130°, partly in order to vulcanise them, and partly to expand the air contained in them. The furrows exhibited by the balls before undergoing this process, get filled out, the sides of the balls are pressed strongly against the interior of the moulds, and retain upon cooling the form assumed during vulcanisation. As it is difficult during the union of the segments to retain sufficient air in the balls to completely expand them during the vulcanising process before the balls are completely closed, a small quantity of water or ammonium carbonate is poured in, which substances exert considerable pressure in the interior of the balls when heated.

Balls, thus prepared, are naturally not very elastic. When very elastic hollow balls are required, they are prepared in the above way, but stronger caoutchouc plates are taken, and they are finally expanded by means of compressed air. In order to effect this, a fine perforation is made in each ball immediately after its removal from the mould, air is forced into the aperture by means of a force pump, and the opening is then closed as quickly as possible with caoutchouc cement. Such balls are often painted of different colours.

Light Gas Balloons require to be made of very thin caoutchouc sheets so that they may rise in the air readily when filled with hydrogen gas under moderate pressure. In order to be effective the weight of the caoutchouc envelope, plus the weight of the enclosed hydrogen gas, must be less than the weight of an equal volume of air. Thus, for instance, supposing the volume of air replaced by the balloon to be 1 gallon, this weighs $\frac{1}{4}$ oz. at the ordinary temperature and pressure, an equal volume of hydrogen under the same conditions weighing only $\frac{1}{56}$ oz., so that when the weight of the caoutchouc envelope is less than the difference between the weight of the air and hydrogen gas (in the above instance $\frac{3}{14}$ oz.) the balloon rises. Referring to the figures just given, if the caoutchouc envelope of the balloon weighs $\frac{1}{7}$ oz., the balloon will be impelled upwards with a force equal to $\frac{1}{14}$ oz.

The thinnest plates of caoutchouc are selected for preparing these balloons, plates of $\frac{1}{25}$ inch thickness, and of the best Para caoutchouc. These plates are cut with the oscillating knife into segments of a form represented by fig. 510. Each segment has an elongation *b a* at one end about $\frac{3}{5}$ in. in length and $\frac{1}{5}$ in. wide. Four segments of the kind are joined together to form a single balloon in the following way. They are heated up to 45° or 50° C. and their edges united by beating them together on an anvil with a hammer in a room having a temperature of 25° or 28° C. The elongation of the segments then forms a tube $\frac{2}{3}$ of an inch long and about $\frac{1}{4}$ in. in diameter, which serves for the filling of the balloons with hydrogen gas.

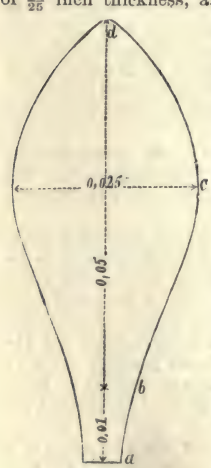


Fig. 510.

The balloons are vulcanised by immersing them for two seconds in a mixture of carbon bisulphide and sulphur chloride containing from 4 to 5 per cent. of the latter substance, and then allowing the carbon bisulphide to evaporate in the air. The balloons are generally coloured by dipping them into a solution of some colouring material dissolved in carbon bisulphide.

These balloons are filled with hydrogen by attaching their contracted ends to an apparatus from which the gas is being evolved, filling them with it under a pressure of 40 inches of water, and then binding the ends securely with thread.

Strong Caoutchouc Rings for the Buffers of Railway Carriages, etc.—Messrs. Aubert and Gérard prepare these rings from a mixture consisting of 100 parts of purified caoutchouc shreds, 5 or 6 parts of sulphur and 5 parts of slaked lime, the materials being combined either in the wolf or by passing them between heated rollers. This product is then rolled out to a strip $\frac{1}{5}$ or $\frac{2}{5}$ of an inch in thickness between a couple of rollers having each a diameter of 20 inches revolving slowly (about 1 revolution per minute) in opposite directions. Immediately upon its departure from the rolling mill, this strip is bound round a hollow roller of sheet iron, the thickness of the rings being dependent upon the number of times the piece is wound round this iron roller. Rings are prepared in

this way, having an outer thickness of as much as 2 inches, which are used for connecting engines and tenders, and also for the buffers of railway carriages, by cutting them with the circular knife. For these purposes especially the best Brazil caoutchouc is to be preferred to the caoutchouc from India or Africa. The vulcanisation of these rings is effected in the usual way either by heating them in iron cylinders by means of steam, or for one or two hours in hermetically closed vessels with water to a temperature of 135°. If the rings are not required to be vulcanised, they are heated for a short time to a temperature not exceeding 100° in order to unite the layers, but this is comparatively seldom the case.

When a heavy caoutchouc mass is required, specifically heavy substances are added in a finely powdered condition, such as heavy spar, lead sulphate, red or yellow ochre, zinc oxide, etc. A greater firmness and tenacity, but less elasticity, is obtained by adding to the caoutchouc heated to 50° or 60° C. from $\frac{1}{10}$ to $\frac{3}{20}$ of its weight of teazed linen rags.

Driving Belts.—These articles are prepared with purified caoutchouc, kneaded up with 5 per cent. of its weight of sulphur between rollers heated to from 50° to 60°, which is pressed into strong linen tissue with such force as to penetrate nearly all the meshes. The machine, called a spreader, is represented by fig. 511. It consists of three hollow rollers (A B C) made of cast-iron, which admit of being heated internally by steam. Each roller has a diameter of 14 inches, and has a toothed wheel attached to one of its extremities. The middle wheel (D) is 9½ inches in diameter, the outer wheels (E E′) are 19 inches in diameter, so that as motion is given to the whole by (D), the wheels (E E′) make only half the number of revolutions executed by (D). The linen strip which is very strong, about 40 inches in width, and from 10 to 50 yards long, is passed together with the caoutchouc between the rollers, which are set very near one another, and it is pressed together by them with such force that the caoutchouc penetrates all the meshes of the linen, causing a very intimate union of the two substances. These impregnated linen pieces are then laid one over another in layers of from 3 to 10, pressed between heated rollers, and cut by a suitable cutting instrument into straps or bands of the required length and breadth. In order to prevent their fraying, as well as to protect their exterior, the bands are covered with linen. In vulcanising these driving belts, they are laid in moulds consisting of a kind of iron gutter with right-angled grooves previously soaped, from which the belts extend at both ends, and into which an iron lid exactly fits, but is about $\frac{2}{5}$ to $\frac{1}{2}$ inch higher than the mould. A number of such moulds are laid together upon a press, the plates of which are hollow and admit of being heated with steam. The press is first of all drawn together, and then steam at a temperature of 140° is let into the press plates. Since iron is a good conductor of heat the belts soon become heated, the operation being complete in an hour. The press is then drawn up, the lids of the moulds removed, and new non-vulcanised portions of the belts are laid in the moulds and treated in the same manner, the operations being continued until the entire lengths of the belts are vulcanised. These bands are very durable, and in respect of price compare favourably with those made from leather.

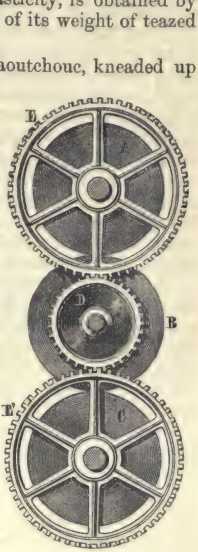


FIG. 511.

Goloshes are made from purified caoutchouc mixed with sulphur and lamp black, and rolled out to a light and somewhat elastic fabric, which is stamped out in patterns and moulded over iron shapes. A shining surface is given to them by covering them with asphalt lac, and they are finally vulcanised while still on the moulds.

A kind of golosh which formerly found its way into the market from America was made by covering moulds with several layers of caoutchouc juice until the necessary thickness had been attained.

Pressing Rollers for dye works are obtained by stretching a strong caoutchouc tube mixed with sulphur over a roller engraved with the required design, and compressing it firmly by linen bands. This is next burnt in an iron cylinder, and finally, when cool, detached, turned inside out and fastened to an even roller.

Elastic Tissues are prepared by weaving thin caoutchouc threads upon looms. Fine caoutchouc threads, the manufacture of which has been already treated of, are softened in warm water, and when very much extended are wound upon bobbins, and exposed for some time to a low temperature. Before weaving, they are generally wound on to other bobbins. The fabric, when complete, consists of very expanded inelastic threads,

and must be heated to 100° to render it elastic, whereupon it contracts just in the same way as a separate thread.

Elastic tissues are also prepared from vulcanised caoutchouc threads. These require considerable stretching when woven.

The industrial applications of caoutchouc are so numerous that it is impossible to detail them all here. The following list gives some of the most important articles made of this substance:—

Ordinary or non-vulcanised caoutchouc is used for making cut sheets for surgical apparatus, and for very thin balloons; cut or rolled sheets for preparing tubes, bands, threads, discs, shoes, balls, etc.; very thin sheets rolled out from heated caoutchouc for preparing waterproof fabrics, cements, varnishes, solvents and plaster; cements and varnishes for joining wood, and for mixing with wool in the manufacture of carpets, and also for book-binding; solid purified elastic blocks for elastic balls, and pieces of india rubber for rubbing out pencil marks. Further, non-vulcanised caoutchouc is used when mixed with linseed oil in the proportion of 2 parts of caoutchouc to 98 parts of oil, for preparing oil for lubricating machinery, and for marine glue, etc.

Vulcanised caoutchouc is used in the manufacture of waterproof fabrics, goloshes, buffers of railway carriages, surgical bandages, garters, straps for binding manuscripts, cravats, etc.; driving belts, air cushions for chairs, sofas, beds, carriages, etc.; water beds for invalids, springs for doors, locks, bells, physical and chemical apparatus, etc.; connecting links of engines and tenders; also for the padding of the sides of billiard tables, for air lids, traps, and for making elastic threads for knitting and weaving. It is further used in the manufacture of rollers employed in dye and printing works, non-corrosive bottles, stoppers, gas and water tubes, solid and hollow balls, etc.; it is also employed for fastening artificial teeth, and for preparing vulcanite, etc.

A very curious application of vulcanised caoutchouc is for the reproduction of enlarged or diminished copies of drawings, etc. This is effected by stretching a plate of vulcanised caoutchouc upon a four-cornered frame, and pressing the drawing upon it. The frame is so arranged that its sides admit of being altered by adjusting screws. Thus, for instance, if it be desired to produce a copy of a picture enlarged four times, the sides of the frame are stretched to double their length. The drawing thus enlarged is then copied upon stone and printed off in the usual way. For preparing diminished copies of a drawing, the frame is expanded, the drawing impressed upon it, and then the frame is drawn together again until the drawing has assumed the required dimensions.

Dialysis of Gases.—Graham and others have shown that all gases do not pass with equal rapidity through the pores of a very thin caoutchouc membrane, that carbonic acid for instance passes through a membrane of the kind with greater rapidity than hydrogen, that oxygen passes through quicker than nitrogen, etc. If a caoutchouc balloon having very thin sides be filled with sawdust, and after the air has been pumped out by means of an air-pump, it be allowed to remain for some time in contact with atmospheric air, it becomes gradually filled with air which contains so large a proportion of oxygen that a glowing match bursts into flame when plunged into it. This air is found upon examination to contain 41·6 per cent. of oxygen, while atmospheric air contains only 21 per cent.

This is a proof that oxygen passes through caoutchouc pores more easily and quickly than nitrogen does. Graham assumed that, upon passing through caoutchouc pores, even permanent gases become liquid, reassuming the gaseous condition upon escaping from the caoutchouc.

Caoutchouc Varnishes and Cements.—For the preparation of caoutchouc varnish or cement, very thin caoutchouc plates are the most suitable. These are cut into small pieces, and placed in closed boxes with from one and a half to two or three times their weight of some liquid which dissolves the caoutchouc either entirely or in part. The

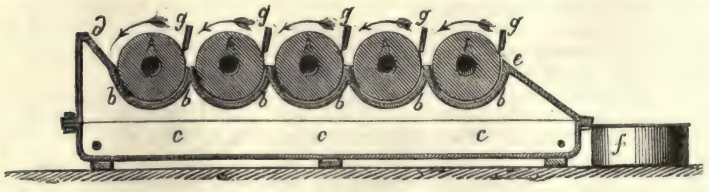


Fig. 512.

solvents generally employed are oil of turpentine or benzol. Caoutchouc, when immersed in either of these liquids for a length of time varying from twenty-four to

forty-eight hours, becomes entirely soft and swells up very considerably; it may be then kneaded in a kneading machine to a perfectly homogeneous mass. A machine of the kind is represented by fig. 512. The rollers (a a) have each a diameter of $4\frac{3}{4}$ inches, and a length of 16 inches; they revolve in the semicircular troughs (*b b*) in the direction of the arrows. The troughs are fixed over a wide iron casing (*c c*) into which steam may be conducted. The softened caoutchouc mass is thrown in at (*d*), seized by the roller and thoroughly squeezed; after passing through it is freed from the roller, liberated by a knife blade (*g*) on the opposite side, and falling down is taken up by the next roller, and so on until it finds its way from the knife of the last roller on to the inclined plane (*e*), and into a vessel (*f*) placed beneath it.

Caoutchouc cement or varnish thus prepared has a more or less viscous consistency, and is used for various purposes; for instance, for connecting india-rubber plates, in the preparation of waterproof fabrics, for covering wainscot work on the side next the wall, for gluing dry pieces of wood in joinery, in the manufacture of musical instruments, and in bookbinding, etc.

Mastic Cement is prepared by heating 2 parts by weight of caoutchouc to 220°, and mixing it when liquid with 1 part by weight of slaked lime. This yields a soft mastic which remains plastic for a long time, and is very suitable for hermetically sealing bottles or other vessels. This method of hermetically closing bottles, etc., was introduced by M. Maissiat, and by its means bottles may be kept hermetically sealed for years. If equal parts of caoutchouc and lime be taken, the result is a solid, but still plastic cement, and if a mastic be required which shall be externally dry and solid, 2 parts of caoutchouc, 1 of lime, and 1 part of litharge are taken.

Machine Grease from Caoutchouc.—An oil is obtained by putting from $1\frac{1}{2}$ to 2 per cent. of caoutchouc into rape seed oil heated to 120° or 130°. The mixture is kept at this temperature for 5 or 6 hours, forming at the end of the operation a dark brown, sticky liquid, which is well adapted for smearing parts of machinery.

Caoutchouc Plaster is prepared by heating caoutchouc to 220°. It forms a sticky, adhesive mass, which has been used successfully to protect wounds from the air.

Manufacture of Vulcanite.—Mr. Goodyear started this branch of industry in America in 1848, and two years afterwards it was introduced into Europe. It has already been mentioned that an excess of sulphur renders caoutchouc hard and less elastic. This fact is taken advantage of in the manufacture of vulcanite. The materials employed in this manufacture are raw caoutchouc from India or Java, and powdered roll sulphur. The raw caoutchouc is submitted to the following process of purification before being mixed with the sulphur.

The raw caoutchouc is softened by immersion for thirty-six to forty-eight hours in water heated to 45° or 50° C., and when sufficiently soft is cut with a knife into long bands weighing each about 2 lbs., and having a thickness of 2 or 4 inches. These are pressed and torn between moistened rollers, which revolve in opposite directions, one making one, the other two revolutions in a minute. The bands thus torn are next further lacerated in a hollander (see p. 641), impurities being at the same time removed by the action of the water. The caoutchouc shreds are now taken out and spread out to dry upon linen frames in a current of warm dry air. Care must be taken that the air is not too warm, or some of the shreds might stick together, retaining water between their interstices.

The dried caoutchouc is pressed and kneaded between rollers heated to 50° or 60° C., so as to form a doughy mass, with which sulphur readily mixes. The proportions used are 100 parts of caoutchouc to 50 parts of very finely powdered and sifted sulphur. When the caoutchouc and sulphur are thoroughly mixed, the two rollers are set apart at a distance corresponding to the thickness of the plate required. The sheets upon coming from the rolling mill are cut into pieces about 16 inches in breadth and 24 inches in length, which are immersed in water at a temperature of about 28° C., in order to give them a certain amount of hardness. They are then again dried and laid upon plates of tin plate or glass smeared with lard. A roller having a horizontal motion is then passed over the pieces of caoutchouc in order to press them against these plates, the caoutchouc being covered with powdered talc to prevent adhesion.

After having been allowed to remain twenty-four hours in a horizontal position, the plates are laid upon iron frames which are placed on supports in such a way that they have an incline of 45°, which serves on the one hand to prevent the caoutchouc plates from slipping when heated, and on the other hand to drain off the condensed water in the next operation. The supports set upon rollers are pushed upon a tramway into a large cylinder of sheet iron, 40 inches in diameter and 20 feet long. This cylinder is closed hermetically by means of a caoutchouc ring fitting in between the edge of the cylinder and a lid of sheet iron, the lid being pressed against the caout-

chouc ring by means of clinches or screws. When the cylinder is closed, superheated steam is conducted into it through a perforated pipe lying along its bottom, and its contents are thereby raised gradually within two or three hours to a temperature of 135° C., which temperature is then kept up for seven hours. When the thicker caoutchouc plates are operated upon, such as are ½ inch thick, the temperature must be raised still more gradually, requiring four hours, and the temperature of 135° C. is kept up for a space of eight hours. The whole is then allowed to cool, and air is admitted into the cylinder, the lid is removed, the supports taken out, and the plates removed from them. The caoutchouc should now be very hard, but still retain a certain amount of elasticity.

When either too great a temperature has been employed, or too much sulphur has been added, the caoutchouc is hard, but it is at the same time brittle and friable. Payen has shown that caoutchouc heated with an excess of sulphur is capable of absorbing as much as 48 per cent. of that substance. A good hard vulcanite, however, should not contain more than 33 per cent. of sulphur.

During the process of heating in the cylinder water is constantly condensing upon the upper part of the cylinder, and drops down upon the caoutchouc plates if these are not properly protected. This is liable to exert an injurious effect on the caoutchouc, owing to particles of rust being carried down along with the water, rendering the surface of the caoutchouc coarse and impure. This may be prevented either by packing the caoutchouc plates between two pieces of sheet iron, and setting them perpendicularly on the supports, or by covering the plates as they lie inclined on the supports with a metal roof which carries away the condensed water.

Plates of vulcanite thus prepared are principally used for making combs. For this purpose after the required shapes are drawn upon them with a piece of pointed steel, they are cut into smaller pieces with a saw. These pieces are then planed on one side, and afterwards rendered smooth by grinding them on tables of slate. The teeth are cut with a circular saw, and polished with pumice powder and tallow. Bent combs are prepared by dipping straight ones into hot water, and giving them the bent form while in the water; they are then dipped as quickly as possible in cold water, and retain afterwards the bent form.

Besides sulphur a number of other substances are employed for hardening caoutchouc, the use of which depends upon the purposes the caoutchouc is afterwards to serve. Thus, for instance, zinc white, white lead, chalk, powdered heavy spar, etc., are sometimes mixed with caoutchouc. For the manufacture of spindles and shuttles, an addition of shellac is made.

Uses of Vulcanite.—The chief use of vulcanite is in the manufacture of combs; combs made of this material having the advantage that they are not injured either by lukewarm or cold water, and do not fray out like horn combs, those made of buffalo horn not excepted, all being of a fibrous nature.

Vulcanite is also used for the disks of electric machines, for furniture, various ornaments, book covers, fans, for corsettes instead of whalebone, for very smooth shuttles, measures, handles of knives, etc.; further for the small silver baths of photographers, for the supports of galvanic batteries, etc.

These articles are coloured either by simply painting them, or the colour is kneaded in with the caoutchouc before vulcanisation.

Manufacture of Artificial Grindstones.—This branch of industry was founded about twelve years ago by M. Deplanque, and since then it has been so much improved that it has now attained considerable importance. The stones are prepared from a composition consisting of quartz sand, powdered flint, emery powder, and caoutchouc dissolved in some cheap oil of tar. This mixture is kneaded together, and yields a product of such durability that it may be used for a very long time without showing much sign of wear. Such stones are well adapted for polishing various implements of wrought iron, steel, cast steel, etc.

The apparatus in which these grindstones are prepared is shown in figs. 513 and 514. A is a boiler (fig. 513) heated from below, the heating of which admits of being easily regulated. About 84 lbs. of caoutchouc clippings are heated in this boiler to 220° or 230° C. In order to facilitate the distribution of heat and the melting of the caoutchouc, 7 lbs. more of heavy oil of tar are added after a lapse of two hours. The caoutchouc gradually melts, and after a lapse of another two hours, another 7 lbs. of oil are added, and this is again repeated in two hours more, so that about 21 lbs. are added in six hours.

The greater portion of this oil of tar evaporates and passes through the iron head B into the tube C, which terminates in a chimney about 100 feet high, so as to carry off the unpleasant-smelling vapour.

When the mixture has become liquid, it is let out through a tube into the receiver E. As vapour escapes here also, the receiver is covered with a capacious head, E',

through which the vapour escapes into the tube C, and finally into the flue. At M is a valve, serving to interrupt the communication between E', the tube C, and the flue.

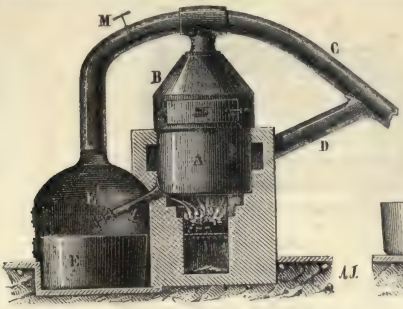


FIG. 513.

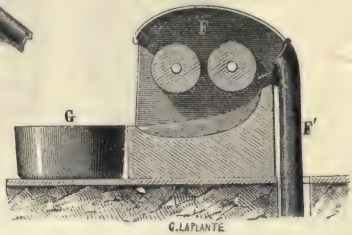


FIG. 514.

The products of combustion from the fireplace pass also through D into C, and into the flue.

The receiver is brought to G (fig. 514), and 28 lbs. of sulphur are stirred up with the caoutchouc mass in it. In order to prevent vesiculation by the formation of sulphuretted hydrogen, 5 lbs. of lime or 10 lbs. of powdered litharge are added to the mixture. 10 or 12 cwts. of powdered quartz, flint, emery, etc., are next added, and a stiff dough is thus obtained, which is then kneaded between the rollers (F) in order to render it homogeneous throughout. The rollers revolve in opposite directions, and the one makes two, the other six revolutions per minute. They have each a diameter of 24 inches, and are heated internally by means of steam to 50° or 60° C. As oil of tar escapes during this process, causing an unpleasant smell, the rollers are covered with a sort of mantle of sheet iron, which conducts the vapours through the tube (F') into the common flue. The caoutchouc mass thus prepared is rolled out to plates of $\frac{1}{5}$ to $3\frac{1}{2}$ inches thick, between two rollers of a similar kind, but having equal rates of revolution (one revolution per minute). These plates are laid on a table strewn with talc powder, and the upper surface of the plates is also covered with the same. By means of a cylindrical cutting machine, fig. 515, disks are cut from these plates, which are covered on their entire surface with powdered talc, and being placed in round moulds under a powerful

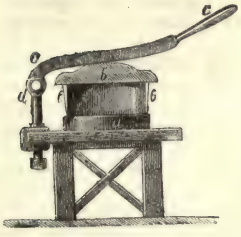


FIG. 515

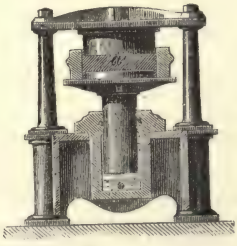


FIG. 516.

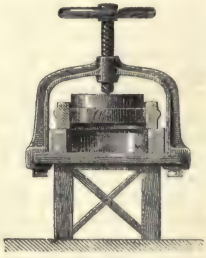


FIG. 517.

hydraulic press, fig. 516, are submitted to a pressure of from 150 to 200 tons. The caoutchouc plates are then forced out of the moulds by means of a screw press (fig. 517), laid again on the table (fig. 515), the irregular edges cut off by the aid of the cutting machine, and a hole is made in the centre of each plate. The disks or plates are next burnt in a cylinder, so as to give the necessary degree of hardness.

The burning is carried out in an apparatus represented by figs. 518 and 519, which consists of a cylinder with a double jacket between which steam is passed through c' under a pressure of 5 atmospheres, and at a temperature of 153° C., so that the temperature of the interior of the cylinder rises to 100° C; the condensed water escapes at c. The interior walls of the cylinder are furnished with supports *b*, *b*, *b*, upon which are placed the iron plates for holding the grinding stones. When the cylinder is fully charged, the lid *e* is screwed up, steam is passed into the double jacket, and

the cylinder kept for seven or eight hours at the temperature of 100°. During the entire course of the operation, an escape of sulphuretted hydrogen takes place together



Fig. 518.

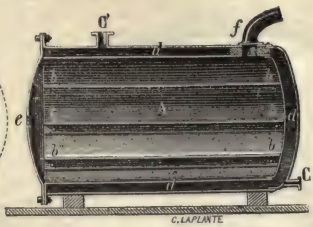


Fig. 519.

with small quantities of vapours of oil of tar, both of which are carried off by a gentle current of air, that enters by a hole in the lid of the cylinder and escapes through a tube at the opposite end. When the burning process is over, the whole is allowed to cool down, and the stones are taken out. As a cylinder of this kind holds on an average half a ton of stones, a ton may be easily burnt in two hours, or in the course of two operations.

The stones thus prepared are fastened upon axes, and are capable of sustaining a rate of rotation of 1,500 or 2,000 revolutions per minute. The largest stones are 2 feet in diameter and 3 inches thick; they weigh about 1½ cwt. each; the smallest are about 1 foot in diameter and ½ inch thick. For sharpening large saws, stones are employed of a thickness varying between ½ and ⅝ inch. For this latter purpose especially the stones seem to be well adapted, and they have a double advantage over files, in saving manual work and being more durable. Besides this application, the stones are much used for grinding and polishing a variety of objects made of wrought and cast iron and steel.

Gutta Percha.—This substance is a product of trees indigenous to Southern Asia, the East Indies, and the Indian Archipelago. It has been long known to the inhabitants of those regions, but its utilisation on a large scale dates from its importation into Europe.

The first notice of it appears to have been in 1842 by Dr. Montgomery, Physician in the Presidency at Singapore, in a letter to the Calcutta Medical Board, and soon afterwards to the East Indian Company, to whom he sent specimens of gutta percha, at the same time alluding to its valuable properties. Dr. Montgomery's priority of discovery, however, was disputed by Dr. Joze D'Almeida, who had also resided for some time in the same locality, and who, on his return to England in 1843, laid specimens of the substance before the Asiatic Society of London, and received an honorary recognition for his services.

Europe had not long discovered the valuable properties of gutta percha before an enormous demand was made for the substance, especially in this country; so great, indeed, that while in 1844 only 4 cwts. were sent over to this country as samples, in the next year as much as 9 tons were imported, and the imports have since risen to thousands of tons.

According to M. Bleekrod's report, there were exported from the Indian Archipelago in 1851 13½ tons, while in 1855 the export from those islands rose to 314 tons.

One consequence of this enormous and sudden increase in the consumption of gutta percha was that every available means was taken to produce great quantities of it as quickly as possible, which eventually led to a complete devastation of the trees yielding it. Collectors of the gutta percha juice appeared on the coast of Sumatra, Java, Borneo, and all the islands of the Indian Archipelago where the trees grow; and, not contented with simply drawing off the sap, cut down whole trees. In this way entire forests were destroyed in the first few years, and it was not until the 'Gutta Percha Trading Society' took the matter in hand, that a simple tapping of the trees was substituted for the former process of felling.

Gutta percha is the chief constituent of the milky juice of the *Isonandra gutta*, Hooker, a tree belonging to the family Sapotaceæ. This tree flourishes in the island of Singapore and in the small neighbouring islands, in Sumatra, on the south east and west coasts of Borneo and Java, and other islands, being found all up the Malayan Peninsula. According to Oxley, the tree grows to a height of 40 to 70 feet, the diameter of the trunk reaching 6 feet. Payen describes the trees as having a height of 65 feet and a diameter of upwards of 3 feet. A tree entirely felled is capable

of yielding as much as from 33 to 40 lbs. of solid gutta percha. The wood of the gutta-percha tree is too soft for use except as fuel.

The milky juice containing the gutta percha circulates in dark-coloured vessels along the stem between the bark and woody pith; in this the gutta percha occurs in the form of globules suspended, but not dissolved, in a watery sap. These globules readily cohere together to form a solid mass.

It appears from an interesting treatise by M. Bleekrod, upon the gutta percha of Surinam, that the price of this article varies considerably according to its quality. The cheapest kind was sold in the Amsterdam market at 3½*d.* per lb., while the dearest cost 1*s.* 4*d.* per lb., sold from the 4,615 cwts. that year imported from the Dutch possessions in the East Indies. M. Bleekrod further showed that the gutta-percha plants admit of being cultivated with advantage in Dutch Guiana, and also that the export from the Dutch Colonies was on the increase, while the exports from Singapore were on the decline owing to the early irrational treatment of the trees.

M. Bleekrod also mentions the production of a substance identical with gutta percha from the *Sapota Müllerí*, a tree also belonging to the Sapotaceous family. He states that the sap is obtained in the same way as from the gutta-percha trees, but that the trees suffer by the process. This substance has now become an article of commerce.

From the researches of M. Payen and others, it appears that ordinary gutta percha consists essentially of three substances, their relative proportions to one another in gutta percha determining its quality. These substances have been termed gutta, alban, and fluavil; and the average composition of gutta percha is:

Gutta	78 to 82 per cent.
Alban	16 to 14 „ „
Fluavil	6 to 4 „ „

According to M. Payen, these three substances may be separated as follows Gutta percha is boiled with absolute alcohol as long as the alcohol dissolves anything, when the residue is pure gutta. The alcoholic liquid contains alban and fluavil; alban is precipitated upon cooling and can be removed by filtration, and the fluavil can be obtained by evaporating the remaining alcoholic liquid.

Pure gutta is insoluble in alcohol, and also in cold ether, but soluble in chloroform and in carbon bisulphide. It is a white substance, melting at 100°, at which temperature thin plates of it are transparent. When cold, such plates are not transparent. Thin strips of gutta percha at a temperature of from 10° to 30° C. are tenacious but not elastic.

In this condition gutta possesses a peculiar property which is taken advantage of in preparing straps, ropes, ribbons, etc. of gutta percha. When, for instance, gutta at the above temperature is stretched out to double its length, it retains upon cooling nearly its extended form. Its structure however becomes essentially altered, passing from a porous into a fibrous condition, while its transparency increases. Gutta percha of the finest quality shows a like behaviour. A band of the latter, $\frac{1}{50}$ inch thick, 1½ inch wide, and 8 inches long, when stretched to 17 inches by attaching to it a weight of 38 oz., does not retain the extended form when the weight is removed, nor even when extended to 25½ inches by a weight of 70 oz., but an elongation of the band $\frac{2}{5}$ inch more by a weight of 75 oz. causes a permanent extension of the band 1¾ inches upon removal of the weight, while at the same time the condition of the gutta percha itself is altered. This experiment was made at a surrounding temperature of 19°.

Pure gutta begins to soften at 50°; thin strips of it become thicker at this temperature, but decrease in length and width. When heated further gutta becomes sticky, assuming between 100° and 110° a doughy consistency, and becoming more transparent. It melts at a temperature of 130°. A still further application of heat causes it to boil, and it yields, as products of destructive distillation, an empyreumatic oil and some gaseous hydrocarbons.

All the three constituents of gutta percha become electrical upon being rubbed, and they are bad conductors of heat. When first thrown into water gutta floats, but it soon becomes specifically heavier by its pores getting filled with water, and then sinks.

As already mentioned, gutta is insoluble in alcohol, and in ether when it has been previously treated with alcohol. It is also very slightly soluble in either benzol or oil of turpentine at a temperature of 0°, but its solubility in these substances increases with the rise of temperature. Carbon bisulphide and chloroform dissolve pure gutta as well as gutta percha at the ordinary temperature.

Pure gutta is not attacked either by the caustic alkalies or by dilute acids; concentrated sulphuric acid or nitric acid, however, exerts a powerful action upon it. Con-

centrated hydrochloric acid acts upon gutta very slowly, colouring white gutta brown, the colour increasing gradually in intensity.

Alban, as already mentioned, separates out from a hot alcoholic extract of gutta percha upon cooling. It forms a white crystalline powder, or sometimes small wart-like lumps. It may be easily obtained in the latter form by allowing its alcoholic solution to evaporate in the air. Examined under the microscope the crystals are seen to be transparent or translucent and in radiating groups. Alban may be heated up to 100° without undergoing any change; it begins to melt at 160° C. and is entirely liquid and transparent at 175° to 180°. When again cooled it contracts considerably, forming a solid transparent mass specifically heavier than water.

Hydrochloric acid, and dilute acids, as well as alkaline liquids, exert no action upon alban, but like gutta it is violently attacked by concentrated nitric acid or sulphuric acid. Alban is soluble in benzol, oil of turpentine, carbon bisulphide, ether, and chloroform. It may be obtained in a crystalline condition from its solutions in the last two solvents, as well as from absolute alcohol.

Fluavil.—This substance is resinous and of a yellow colour, a little heavier than water, and hard and brittle at a temperature of 0°. At higher temperatures it is soft; at 60° it assumes a doughy consistency, melting completely when heated to 100° or 110°. When exposed to a still higher temperature it boils, at the same time undergoing decomposition, the products of its distillation consisting of acid vapours and a number of different hydrocarbons. Fluavil is soluble in hot and cold alcohol, also in ether, oil of turpentine, carbon bisulphide, and chloroform. When its solutions in these solvents are evaporated, fluavil is deposited in the amorphous condition only. As obtained by evaporation from an alcoholic solution it retains very energetically the last portions of the solvent, from which it can be separated only by protracted heating at 100°C. Fluavil is not attacked either by dilute acids or solutions of caustic alkalies, but is attacked energetically by concentrated nitric acid or sulphuric acid.

Gutta percha being a mixture of the three substances gutta, alban, and fluavil, its properties may be deduced from a consideration of those of these three bodies. Gutta percha is not attacked either by alkaline liquids or by dilute acids, a fact of considerable importance for the industrial applications of this substance, since it follows that most liquids such as wine, beer, vinegar, soda ley, etc, are without action upon it. Gutta percha is, however, energetically attacked by concentrated nitric acid, yielding upon protracted boiling with this reagent nitric oxide, nitrous acid, camphresinic acid, and other products of oxidation. Concentrated sulphuric acid causes gutta percha to swell, and converts it into a mucilaginous mass. Although concentrated hydrochloric acid attacks gutta percha only slightly, still the gutta percha syphons employed in manufactories of this acid suffer considerably in course of time.

One of the most valuable properties of gutta percha is that of becoming soft and plastic when moderately heated. At the ordinary temperature it is tenacious and stiff, but becomes pliant when heated to 25°, begins to soften at 48°, and is so plastic between 55° and 60° that it may be moulded into any desired form.

Results, differing in many respects from those of M. Payen, have been obtained by M. Baumhauer. He has come to the conclusion that the chief constituent of gutta percha is a hydrocarbon having a composition represented by the formula $C_{10}H_{16}$, besides various products of its oxidation, two of which he has determined with certainty and represents by the formulæ $C_{20}H_{32}O$ and $C_{20}H_{32}O_2$. The opinion of M. Baumhauer is that only the first of these three substances, $C_{10}H_{16}$, is contained in the fresh gutta-percha sap, and that this is identical with the gutta of M. Payen. The other two oxygen compounds which occur in gutta percha, together with small quantities of a number of other similar products, he considers to be the results of the oxidising influence of the air upon the pure sap.

M. Baumhauer prepares pure gutta by treating gutta percha first with water and hydrochloric acid respectively, and then with boiling ether. The ether dissolves everything except a brownish-black substance, which is quickly filtered off, the gutta separating from the filtrate upon cooling in the form of a white powder. This powder is then recrystallised from ether until, upon cooling, nothing more remains dissolved.

When exposed to the air, gutta percha undergoes a peculiar change, which is especially noticeable when the air has a temperature of 25° or 30°, and the gutta percha is in the form of thin plates, ribbons, or threads. The gutta percha emits a peculiar smell, which is accompanied by the evolution of acid vapours, while the substance assumes a yellowish colour. This change is very injurious, for it is accompanied by a loss of tenacity, hardness, and pliancy in the gutta percha itself, the gutta gradually disappearing, a fact which may be verified by treating such altered gutta percha with cold absolute alcohol, in which it dissolves after a lapse of some time. On this account many attempts have been made to protect gutta percha from this destructive influence

of the air. It may be conveniently preserved under water in vessels of wrought or cast iron, probably because the iron deprives the water of the oxygen dissolved in it. Ozonised air exerts a strongly oxidising effect upon gutta percha. Gutta percha is especially quickly oxidised when exposed to a moist atmosphere under the influence of the sun's rays.

The method of obtaining the sap of gutta-percha trees formerly employed, consisted in felling the trees, making incisions in the bark at distances of from 1 to 1½ feet from each other, and then collecting the juice in vessels placed beneath such incisions. The method now employed is simply to make incisions in the stems of living trees and to collect the juice in hollows at the foot of the trees. The juice coagulates in a short time, and is then kneaded with the hands, formed into various shaped blocks, and sent to Europe, packed in coarse wrappers.

The raw gutta percha of commerce contains a number of mechanical impurities, such as pieces of woody fibre, earthy mixtures, etc., which have to be got rid of before the gutta percha can be worked. The process of purification is executed by the aid of a specially constructed apparatus. The gutta percha is first of all cut into shreds by a machine consisting of a large disk, fitted with three straight or curved planing irons in such a way that upon turning the disk the pieces of gutta percha lying upon the inclined surface, and slightly pressed against the revolving disk, are planed into delicate shreds. The planing irons are kept wet with water during the operation. The gutta percha passes from this cutting machine on to a shelf, when it is pressed by means of two rollers against a drum furnished with saw teeth similar to that used in cutting beet roots in sugar manufactories (see SUGAR), and cut into still finer pieces. From this shelf the pieces of gutta percha fall into a basin filled with cold water, where the ligneous particles, absorbing water and becoming heavier, fall to the bottom, the other impurities are dissolved out by the water, while the gutta percha itself floats on the surface. Here it is caught by an endless cloth, stretched upon two rollers, pressed upon a second drum, passed into a second water basin, and then to the third cutting machine, which may either have the form of the two former ones, or it may consist of a hollander (see p. 641). The gutta percha after this finds its way into a large basin filled with water at a temperature of 80°, then is brought by the agency of an endless cloth under a drum, furnished with knife blades, and between it and its breasting, also armed with knife blades, it is once more submitted to a cutting and tearing process.

This last tearing and the action of the hot water serve to aggregate the pieces of gutta percha, admitting of its formation into blocks. For this purpose it is carried upon an endless cloth between five pair of rollers, which are so set that the lower one of each pair revolves underneath water, and the upper one just on the surface. The rate of revolution of the rollers increases towards the last pair. The gutta percha is converted into a long band, and passes from the bath upon the endless cloth, between another pair of rollers, which press out adherent water from it. The gutta percha is then either rolled out directly into plates by a rolling mill, or into round or angular threads, bands, etc., by means of a grooved mill, the rollers being set in equal but opposite motion.

In Mr. Hancock's manufactory, the gutta percha is purified by placing the shreds in water heated to 100°, and violently agitated. The shreds become sticky, and are then pressed into balls. These balls are placed in a cylindrical vessel in which revolves a toothed roller which again tears it into very fine pieces. The pieces are washed with water to separate the impurities which fall to the bottom.

Upon leaving the washing apparatus, the gutta percha is rolled out into plates, which, when required for moulding, are softened by gentle heating. This heating is effected by placing the gutta-percha plates in a semi-globular vessel of iron with double sides, between which steam is passed at a temperature of 153°, and under a pressure of 5 atmospheres, and this serves to heat the gutta percha to 112° or 115°. The gutta percha is thus not only rendered soft and plastic, but adherent water is driven off, and a material is obtained which is more durable, and admits of being more easily and firmly united.

M. Payen proposed the use of spirit of wine, where it can be had cheaply, for purifying gutta percha, injurious substances such as alban and fluavil being dissolved out by the spirit. To prevent loss of alcohol he recommended further the use of the apparatus referred to in the description of the extraction of fatty oils by carbon bisulphide (see p. 144).

The following alterations and improvements in the method of purifying gutta percha have been introduced by M. Leverd.

The complete division of the gutta percha is effected by a machine depicted in figs. 520 and 521. Blocks of gutta percha are cut with a circular saw into irregular prisms, and then pressed against a tearing drum upon a table (D). The drum has a

width of 6 inches, and a diameter of 12 inches, and is covered on its exterior surface with rows of strong, sharp steel teeth in such a way that the teeth of one row face

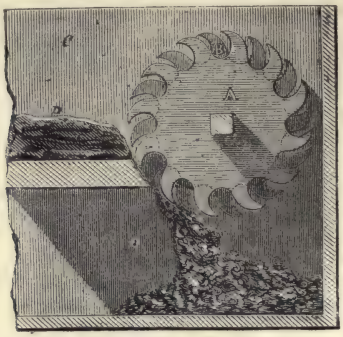


Fig. 520.



Fig. 521.

the divisions between the teeth of the second row, etc., as shown in fig. 520. The tearing operation is assisted by a stream of water flowing over the drum which is kept slowly revolving.

The torn shreds of gutta percha are next washed in three vessels, communicating with one another either by syphons or straight tubes. The wash water passes from the third tub or basin into the second, and from the second into the first, from whence it is then run off, so that in this way the washed gutta percha comes into contact with water increasing in purity.



Fig. 522.

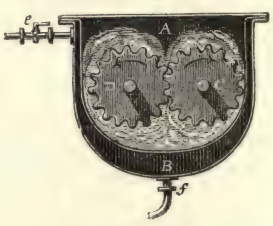


Fig. 523.

The washed gutta-percha mass is then spread out upon an inclined floor for the water to run off. It is further dried by passing it through a rolling mill, the rollers of which are heated internally by steam. The gutta percha issues from between the rollers in very thin plates, which are at once seized by workmen, who stretch them out to double their width; any particles of ligneous fibre that they may still contain are in this thin condition of the plates easily detected and picked out. The sheets or plates are then spread out in the air for a short time to effect a further drying.

The last traces of moisture are removed by heating in an apparatus represented by fig. 522, consisting of a flat vessel A with double sides B, into which steam is passed through the cock C, and the contents of the vessel thus heated up to 110° or 115° C. The condensed water escapes through D back again into the boiler. The shallow vessel A is fitted with a lid consisting of three movable pieces, which arrangement admits of an easier filling and emptying of the vessel than if the latter were made of a single piece. When the gutta-percha mass has been so long heated in this apparatus that no more moisture is driven off, it is next passed into the kneading machine (fig. 523), which consists of an elongated vessel A (shown in the fig. in section). In this vessel rotate two grooved rollers C and D, the grooves of which fit into each other. The rollers revolve in opposite directions, as shown by the arrows, and effect a thorough kneading of the mass, which latter is kept of a doughy consistency by steam passed through the cock *e*, into the jacket of the kneading vessel, the condensed water returning to the boiler by the pipe *f*.

The kneading of the gutta percha to a homogeneous mass in this apparatus is generally effected in the course of an hour, and it is then passed into a rolling mill, which rolls it out into bands, straps, ropes, threads, etc.

The gutta-percha dough obtained by the aid of this apparatus is especially suitable for the preparation of round ropes or tubes with the vermicelli press.

In the manufacturing of ropes and tubes of gutta percha, a jacketed cylinder, heated with steam to 100°, is charged with gutta-percha dough. By means of a closely fitting piston entering at one end of the cylinder, the dough is pressed out through a conical mouthpiece at the other end, and thus receives the desired form. The tubes first pressed out are put on one side, as they are vesiculated by the air originally contained in the apparatus. The tubes pass from the aperture into a trough filled with cold water, by which they are sufficiently hardened to retain their form.

Firmer and more compact tubes are obtained by moulding the gutta-percha mass first into wide tubes, and stretching these out to twice their length. To avoid the loss of time in the frequent filling of the apparatus, and the disadvantage of introducing air into the cylinder with each supply of material, causing a vesiculation of the tubes, Messrs. Nichols and Selby use, instead of a piston, a pair of rollers moving in opposite directions and pressing upon the gutta-percha mass in the cylinder. The dough is supplied through the rollers in quantities exactly corresponding to that passing out at the aperture in the form of tubes, etc. The action is thus continuous, and tubes of any required length may be made.

Round threads of gutta percha are prepared by a method exactly corresponding to that employed in the manufacture of round threads of caoutchouc.

Plates of gutta percha are also prepared by a process similar to that employed in the manufacture of the same articles in caoutchouc, the only difference being that plastic gutta percha heated to 100° or 115° is used.

Ribbons and angular threads are prepared from gutta-percha plates by cutting them lengthways with sharp-pointed knifes set against the drawing rollers. The width of the ribbons or threads depends upon the distance the knives are set apart from each other. The still soft ribbons or threads are passed over an endless cloth so as to cool them.

Gutta-percha mouldings, impressions of medals, etc., are obtained by pressing the plastic gutta percha into moulds or upon the surfaces to be copied, and allowing it to cool.

Vulcanisation of Gutta Percha.—As gutta percha becomes so soft at a temperature of 45° to 60° that it cannot be used for machines in warm rooms, or for reins, etc., attempts have been made to vulcanise it, and it has been found that gutta percha, like india rubber, undergoes a peculiar change when heated with sulphur.

For vulcanising gutta percha the hyposulphites of lead or zinc are more suitable than sulphur itself. A mixture of 100 parts of gutta percha with 15 parts of the hyposulphite is kneaded at a temperature of 100°, and the moulded object made from this is afterwards heated to 140°.

A number of other substances have also been proposed for mixing with gutta percha so as to modify its properties. Mr. Hancock recommends an addition of caoutchouc for preparing ribbons, straps, etc. Mr. Forster recommends an addition of 1 part of bone black to 4 parts of gutta percha for making a varnish for clothes, leather, etc. He also recommends for pressed manufactures the following mixture :—

Gutta percha	4 parts
Bone black	2 „
Arsenious acid	$\frac{1}{16}$ „

A very hard mass is yielded by—

Gutta percha	3 parts
Powdered bones	1 „
Pipe clay	$\frac{1}{2}$ „

Insulation of Telegraph Wires with Gutta Percha.—Siemens was the first to employ gutta percha for the insulation of telegraph wires, but his method has not been found efficient for subterranean lines, owing to the insulating material being eaten by animals. This kind of insulation has been found very serviceable, however, for submarine telegraphs, and it is that adopted, among other instances, in the submarine telegraphs between Europe and America.

The copper wire is covered by means of an apparatus similar in construction to that already described for pressing gutta-percha tubes, a perforated block through which the wire is drawn being set against the moulding aperture, and as the wire passes through it is covered with gutta percha. The wire is in this case drawn out by the friction of the gutta percha itself. When several wires have to be covered at the same time a block is employed, having the required number of perforations, through which the wires are drawn.

The Atlantic cable laid in 1858 consists of a nucleus of 7 copper wires, 6 lying round a middle one. This nucleus of wires is surrounded by a threefold covering of gutta percha; this again by a stuffing of hemp soaked in tar, and round this is finally wound spirally 18 strands of soft iron wire.

The cable of 1866 consists also of a nucleus of 7 copper wires, surrounded by Chatterton's compound; over these are wound 4 coats of gutta percha, alternating with 4 coats of Chatterton's compound, and finally 10 strands of galvanised iron wire, each being surrounded with jute yarn saturated with tar. The Atlantic cable of 1865 is of similar construction.

The insulation of the French Atlantic cable is nearly the same as the above, consisting of 4 coats of gutta percha with intermediate layers of Chatterton's compound. The nucleus also of 7 strands of copper wire is, however, thicker than in the previously mentioned cables. The external coating consists of galvanised wires of Bessemer steel covered with yarn.

GUM.

Gum is the general name for a number of allied carbohydrates which frequently occur in plants, especially various species of acacia, and exude from the trees in the form of transparent tears. Various fruit trees, such as the plum and cherry, furnish a similar product. The seeds of various plants also contain a kind of gum, which differs from the gum arabic, gum senegal, cherry tree or native gum, gum of Bassora, and gum tragacanth, by being insoluble even in boiling water, only swelling up into a gelatinous mass. The various kinds of gum form a thick glutinous solution with water, and are insoluble in alcohol. By oxidation with nitric acid, they are converted into oxalic and mucic acids.

Until the year 1860, when Fremy published the results of his investigations, gum was looked upon as a neutral substance, analogous to dextrin, but intermixed with some organic matters. Fremy, however, came to the conclusion that the different kinds of gum are compounds of bases with modifications of a gelatinous substance, comparable to the pectic compounds derived from pectose. The following are the principal grounds upon which he based his conclusions.

When a solution of gum arabic is treated with oxalic acid and lime eliminated, there remains in solution an organic substance which Fremy considered to be a weak acid, and he named it gummic acid.

When a very thick aqueous solution of gum arabic is left for several hours in contact with concentrated sulphuric acid, so as not to mix, the previously soluble gum becomes transformed into a kind of membrane which is insoluble even in boiling water. This is an isomeric modification of the previously mentioned 'gummic acid,' and has been named metagummic acid. This change does not take place when dilute sulphuric acid or simply powdered gum is used.

Upon heating the insoluble metagummic acid with traces of an alkali, it is immediately dissolved, and is no longer precipitated by an acid; the metagummic acid having been reconverted into gummic acid, which remains in combination with the alkali used. When lime is employed, the product presents all the characters of gum arabic. On the other hand, when the gummic acid set free by oxalic acid is heated, it is converted into metagummic acid, and when this in its turn is treated with lime, gum arabic is regenerated.

Gelis had observed that, under the influence of a temperature of 150° C. maintained for several hours, gum arabic becomes insoluble in water, and that after boiling it for several hours in water it again becomes soluble. This is explained by supposing that, under the influence of heat, insoluble metagummate of lime is formed, the lime remaining in combination, and that, under the influence of boiling water, soluble gum (gummate of lime) is regenerated.

Cherry tree gum contains a substance soluble in water, and identical with gum arabic, together with another insoluble in water, called cerasin, identical with Gelis's metagummate of lime, obtained by heating gum arabic, and like it becoming soluble after prolonged boiling in water. From the fact that cerasin is occasionally met with ready formed in some kinds of fruit, and from other considerations, Fremy considered it probable that the insoluble body is first formed naturally, and that the soluble modification is the result of the subsequent influence of vegetation.

Bassora gum is almost entirely insoluble, a portion consisting of a gelatinous substance presenting many analogies with metagummic acid, but not identical with it. When treated with alkalies or alkaline earths, it yields true gum soluble in water, insipid, uncrystallisable, and insoluble in alcohol, but differing from gum arabic in being precipitated by neutral acetate of lead.

Fremy suggests that the facility with which the conversion of soluble gum into an insoluble condition takes place may allow of the use of gum as a substitute for albumin in fixing colours.

Gum Arabic exudes from several kinds of acacia, such as *A. vera* and *A. arabica* of Egypt and Arabia. The tears are either white or slightly yellow or brown, and

crack on exposure to the air. If this gum be dissolved in water, acidulated with hydrochloric acid, and mixed with alcohol, white flakes of arabin or arabic acid, $2C_6H_{10}O_5.H_2O$, or $C_{12}H_{22}O_{11}$ (the gummic acid of Fremy), are deposited.

Gum arabic consists of soluble calcium, magnesium, and potassium gummates. Gummic acid dried at 127° C. becomes $C_{12}H_{20}O_{10}$ by loss of H_2O. Gum arabic has a specific gravity of 1·355, and contains 70·40 per cent. arabin and 17·60 per cent. water; the remaining 12 per cent. is made up of combined bases, acid calcic malate, etc. A solution of the gum produces left-handed rotation of a polarised ray, and is not susceptible of alcoholic fermentation by means of yeast, but if digested with cheese and chalk, it may be made to furnish 12 per cent. or more of alcohol; calcic lactate is simultaneously formed. Dilute sulphuric acid changes gum arabin into dextrin, and this on boiling becomes dextro-rotatory sugar capable of being fermented. A sulpho-gummic acid is produced by the action of strong sulphuric acid upon gum arabic. When oxidised with nitric acid it yields not only oxalic acid and mucic acid, but also saccharic and tartaric acids; with fuming acid, substitution compounds are produced.

Gum arabic is much used in medicine for the preparation of emollient pastes and syrups; it is also used in the preparation of inks to sustain the suspension of the tannate of iron. For thickening colours, etc., it is also largely employed.

Gum Senegal from *A. Senegal* shows a specific gravity of 1·436, and contains 81·10 per cent. arabin, 16·10 per cent. water, and 2 or 3 per cent. saline matters. It is mainly used by calico printers for thickening colours and mordants.

Cherry-tree Gum exudes from trees of the amygdalaceous order. It is only partially soluble in water, and consists of 52·1 per cent. arabin, 34·9 per cent. cerasin (a metagummate of lime), 12 per cent. water, and 1 per cent. saline matters.

Bassora Gum appears to be furnished by a cactus. The soluble part constitutes about 1 per cent. of the gum; the insoluble *bassorin* dissolves in weak alkalies and acids by means of heat.

Gum Tragacanth exudes from the *Astragalus verus* of Armenia and Persia. Its sp gr. is 1·384, and about 50 per cent. dissolves in cold water; the insoluble part swells up and has been shown to contain starch. Warm dilute acids effect the entire solution of gum tragacanth, and boiling water dissolves it almost entirely.

The soluble portion of tragacanth, although closely resembling the arabin of gum arabic, differs from it in not giving any reaction with silicate of potash or perchloride of iron, and in the appearance of the precipitate produced by alcohol. For this reason it has been sometimes distinguished from the arabin of gum arabic as tragacanthin. The insoluble portion has generally been described as bassorin, but some recent researches of Giraud appear to indicate that it consists largely of an insoluble pectic principle, probably pectose. When digested with fifty times its weight of water for several hours in a water bath, it becomes partially soluble, and loses its property of swelling after drying. Submitted to the action of acidulated water (1 per cent.), it becomes entirely soluble. The new product is principally pectin, combining with alkalies to form pectates and metapectates that are precipitated by alcohol. By treatment of the barium compound with hydrochloric or acetic acid, pectic acid is set free. According to Giraud, the composition of gum tragacanth is:—

Water	20	per cent.
Pectic compound	60	„
Soluble gum	8–10	„
Cellulose	3	„
Starch	2–3	„
Inorganic matter	3	„
Nitrogenous bodies	traces	

It is used in medicine and calico printing, and also by shoemakers.

Mucilage, or the gum of seeds and roots, appears to be an almost universal constituent of plants. It is extracted by steeping the seeds and roots in hot water, when a jelly is formed consisting of swollen cells containing mucilage in solution. Dilute acids at 100° furnish from this product glucose.

Gum from Sugar.—According to Reichardt, a gum is produced and accompanies gummic acid when glucose is oxidised by cupric salts. The formula $C_{12}H_{26}O_{13}$ has been assigned to it.

Artificial gum, known as British gum and dextrin, is produced by the torrefaction of starch.

STARCH.

Occurrence.—Starch is a substance closely related to cellulose, having the same percentage composition and similar properties. It does not occur in such large quantities as cellulose, but quite as frequently; and probably all phanerogamous plants contain starch at some period of their growth.

Starch occurs in relatively larger quantities in many of the organs of propagation, such as tubers and rhizomes; in potatoes, the seeds of cereals, the fruit of chestnuts, etc., and it serves as food for the young plant in the first stages of its growth, being dissolved and assimilated until leaves have been developed, and the plant becomes capable of taking its nourishment from the air and soil.

Starch also occurs in many other parts, as in the pith of trees and shrubs, in woody and parenchymatous tissues, etc. Its occurrence in these parts is not, however, constant and equal, the same tissues being at certain seasons fully charged with starch, and at others almost entirely devoid of it. During the period of active growth plants produce from inorganic substances organised material in greater quantity than they require. Part of this material assumes the form of starch, and is stored up for use when, at a future time, in the formation of new substance, the plant can no longer obtain food from external sources. Other substances similar to starch, such as sugar, inulin, etc., serve the same purpose in the plant.

Characters.—Starch in its earliest condition, as it originates in plant cells, always forms hard round granules which exhibit a peculiar process of growth; dissolved substances formed by the chemical agency of the protoplasm being absorbed, converted into starch, and deposited in such a way that these substances are uniformly distributed in all directions throughout the entire mass of the granule. The growth of a starch granule is not, as was at one time supposed, similar to the growth of a crystal, in which the new substance arranges itself symmetrically around a nucleus, neither are new layers deposited in the interior of the original granule, or by apposition, but in the way described, by intussusception.

As the growth increases, a peculiar alteration takes place in the substance. The original nucleus appears under the miscroscope as a homogeneous mass; but the growing granule becomes stratified, owing to layers arranging themselves concentrically or excentrically round a nucleus. Every granule contains one or more nuclei, each of which is surrounded by a number of layers. This stratification depends upon the degree of density of the material, and the density varies with the different amount of water in each layer, the result being that a layer rich in water always alternates with one poor in water. The external layer is always dense, containing but a small quantity of water; next to this is a layer richer in water and less dense, and so on until the nucleus itself is reached, which always contains a proportionately large quantity of water.

The nuclei of starch granules are surrounded on all sides by layers, but this stratification is not equally perceptible in all kinds of starch; it is easily seen in the large starch grains of the potato tuber, and those obtained from the fruit of the potato are still better for demonstrating this appearance. Fig. 524 represents starch grains that have been crushed by pressure. A similar appearance is presented by starch grains that have been heated to a temperature of 200° or 210° and then moistened with water. Fig. 525 represents starch grains that have been thus treated, and the stratification may be easily seen.



Fig. 524.



Fig. 525.

The growth of starch granules is not alike in all plants, one plant yielding larger granules than another; in some plants the granules are round, in others they are lenticular; some are irregularly round; many are polyhedral, being partly flattened by

the pressure of other granules; others are club-shaped. The origin of most starches can be determined by their form, and some of the principal varieties of starch met with in commerce are represented by the following illustrations taken from Hassall's work on 'Food.'

Potato starch, represented by fig. 526, as magnified 200 diameters, has the form of ovate or oyster-shaped granules, exhibiting distinct concentric rings. The hilum is well defined, but small, and is situated at the narrow end of the granule.

Maranta starch, or West India arrowroot, obtained from the rhizomes of *Maranta arundinacea*, is represented by fig. 527, as magnified 240 diameters. The

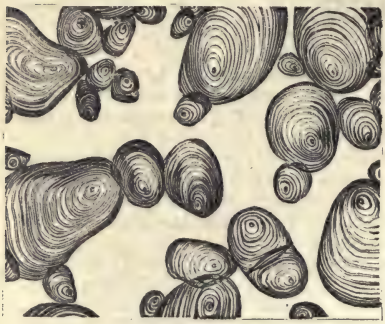


FIG. 526.

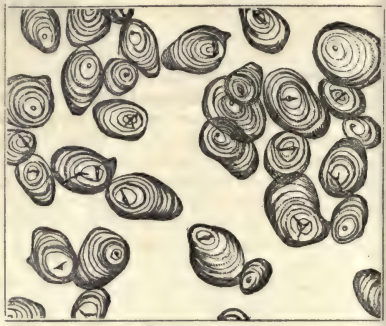


FIG. 527.

granules are generally oblong or ovate, sometimes mussel shaped, or even to some extent triangular. The size of the granules varies considerably. They present distinct concentric lines and the hilum is well defined, in most cases as a distinct transverse line, which is specially characteristic of this kind of starch, less frequently as a circular spot.

The starch obtained from *Canna edulis*, and commonly known as tous-les-mois arrowroot, is represented by fig. 528, as magnified 225 diameters. The granules are



FIG. 528.



FIG. 529.

very large, ovate, flat and broad, and sometimes pointed at the narrow end. They exhibit distinct concentric rings, which are very fine, regular, and close together. The granules vary considerably in size, but they are generally much larger than those of potato starch, and the hilum is less distinctly marked.

The starch known by the name of sago is obtained from the pith of several kinds of palm, growing in the islands of the Indian Archipelago, Madagascar, and New Guinea, *Sagus Rumphii*, *S. farinifera*, *S. raphia*, *S. lævis*, and *S. genuina*; also from *Cycas circinalis* and *C. revoluta*, growing in China and Japan. The granules of this starch are represented by fig. 529, as magnified 225 diameters. They vary in size, are elongated, rounded at one end, and truncated at the other. The hilum is sometimes circular, but often presents the appearance of a transverse slit or star. The concentric rings are generally indistinct, and sometimes the granules have a somewhat corrugated appearance.

Tacca or Tahiti arrowroot consists of the starch obtained from the tubers

of *Tacca oceanica*, a native of the South Sea Islands. The granules of this starch are represented by fig. 530, as magnified 220 diameters. They somewhat resemble those of sago starch, having similar rounded and truncated ends, but are generally very much smaller and less elongated. The concentric rings are very indistinct. The hilum is generally circular, but sometimes presents the stellate form observed in sago starch.

The starch obtained from the tubers of *Curcuma angustifolia*, and commonly known as East India arrowroot, is represented by fig. 531, as magnified 240 diameters. The granules are flat, elongated, and irregularly shaped, usually with one

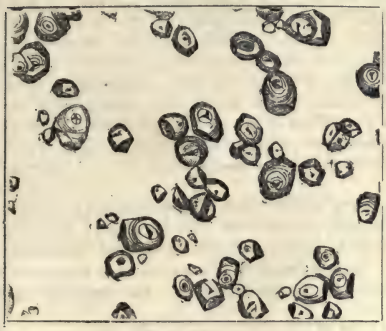


Fig. 530.



Fig. 531.

end pointed and the other obtuse. The hilum, situated at the pointed extremity, is very indistinct and sometimes not recognisable. The concentric lines are frequently interrupted. The granules are generally larger than those of West Indian arrowroot, and in several other respects these two kinds of starch are easily distinguishable.

The starch obtained from *Manihot utilissima*, *M. Aipi*, and *M. Janipha*, known as Brazilian arrowroot and tapioca, is represented by fig. 532, as magnified 225

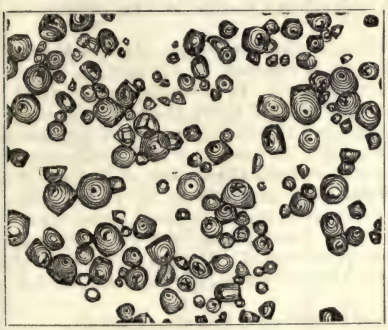


Fig. 532.

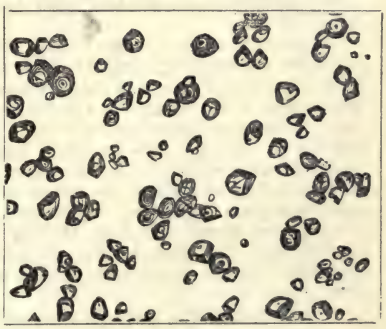


Fig. 533.

diameters. The granules are small, and sometimes two or more are united together. They frequently present truncated surfaces. The hilum is distinct, generally circular, but sometimes stellate.

The starch obtained from the tubers of *Arum maculatum*, and commonly known as Portland arrowroot, is represented by fig. 533, as magnified 240 diameters. The granules present considerable resemblance in configuration to those of tacca arrowroot, having the truncated surfaces, the fissured or stellate hilum and indistinct rings, but are very much smaller, and are thus easily distinguishable from them.

The starch obtained from the different sources above mentioned, with the exception of potato starch, is met with in commerce under the name of arrowroot, of which there are several kinds, presenting slight differences in their characters, and in the facility with which they are converted into paste by hot water, on which account they have a higher value than potato starch. Potato starch, rice starch, and maize starch are also commonly met with, but they are generally inferior to those kinds known as arrow root. For illustrations of the granules of these and some other kinds of starch, see article 'Bread.

It has been established by the researches of Nägeli, confirmed by many others, that starch granules consist of two substances chemically different, but having a like composition.

If certain solvents, such as saliva at a temperature of 40° to 47°, dilute extract of malt, or very dilute acids, be allowed to act on starch for some time, the greater part of it is dissolved. The undissolved residue is a little reduced in volume, but otherwise apparently unaltered, the stratification being more distinct than before. The residue when treated with a solution of iodine shows a different deportment from that of the original granules; these are at once coloured intensely blue by iodine, while the residue does not show that reaction provided the solvents have been allowed to act long enough. The coloration, however, takes place immediately if the residue be first treated with a drop of concentrated sulphuric acid. Starch, therefore, consists of an easily soluble substance, coloured blue by iodine, and an insoluble substance, which is only coloured blue by iodine after the addition of sulphuric acid, behaving in this respect like cellulose. Nägeli accordingly distinguishes these two constituents as starch cellulose and starch granulose. The granulose is present in relatively greater quantity, and to it the unaltered starch owes the property of becoming blue with iodine. Both substances are distributed throughout the entire mass of the starch granule, and are not separated in layers.

Unaltered starch granules are at the ordinary temperature and pressure insoluble in water. But starch absorbs water in different proportions, and retains it so persistently that Payen was on this account led to assume the existence of different chemical compounds of starch with water. Starch dried in a vacuum at a temperature of 120°–140° is anhydrous. In this condition Payen represents the composition of starch as:

$$C_{12}H_{18}O_9.H_2O \text{ or } 2C_6H_{10}O_5,$$

in which the molecule of water is considered as water of combination replaceable by bases. Anhydrous starch is a very mobile powder, of exceedingly hygroscopic nature. It absorbs moisture with great rapidity from the air, passing into the first hydrate, which, besides the water of combination, also contains a further two molecules of water according to the formula:

$$C_{12}H_{18}O_9.H_2O + 2H_2O \text{ or } C_6H_{10}O_5H_2O.$$

This compound is also obtained when starch is dried in a vacuum at a temperature of 10° to 15°.

When exposed for a longer time to the action of the atmosphere, starch takes up two more molecules of water, in which condition it contains 18 per cent. of water. This is the amount present in ordinary commercial starch. In an atmosphere saturated with moisture the absorption extends to 10 molecules of water, the resulting compound containing 35 per cent. of water. In this condition the granules stick together, and can be made into balls by simply kneading with the hands. A still further compound of starch with water, called **green starch**, contains 45 per cent. of water. It is obtained by absorbing the excess of water from starch paste by placing the paste on a plate of gypsum. Upon throwing this green starch, in small quantities at a time, upon plates heated to 140° or 150°, the granules suddenly swell up and agglutinate. This property of starch is taken advantage of industrially in preparing from potato starch imitations of certain exotic kinds of starch, known in the market as **tapioca**.

The following table gives the composition of the different hydrates of starch:

	Formula	Percentage Composition	
		Anhydrous Starch	Water
Anhydrous only in combination .	$C_{12}H_{18}O_9$	—	—
Dried in vacuum at 150° . .	$C_{12}H_{18}O_9.H_2O$	100	—
Dried in vacuum at 15° . .	$C_{12}H_{18}O_9.H_2O + 2H_2O$	90	10
Air dried	$C_{12}H_{18}O_9.H_2O + 4H_2O$	81·82	18·18
Kept in moist atmosphere . .	$C_{12}H_{18}O_9.H_2O + 10H_2O$	64·39	35·71
Green starch	$C_{12}H_{18}O_9.H_2O + 15H_2O$	54·55	45·45

It appears very doubtful whether these hydrated starch compounds can be properly considered as chemical compounds, since the water is so loosely combined that the slightest change of temperature, indeed every change in the atmospheric moisture, causes an expulsion of part of their water or *vice versâ*. Payen's dry starch may be considered as a constant compound, having a composition represented by the formula

$C_{12}H_{20}O_{10}$. This substance is hygroscopic, retaining with more or less energy the absorbed water just like wool, silk, and many vegetable substances. It is possible that a part of the water is held by simple surface attraction, while the other part is held by the power of absorption of the less dense layers of the granules.

For the determination of the amount of water in a sample of starch Scheibler has given a method which may easily be employed. It is based upon the fact that starch which contains more than 11·4 per cent. of water readily parts with the excess when treated with alcohol of ·8339 specific gravity, while starch containing less water takes up from alcohol of the above strength water sufficient to bring the amount up to 11·4 per cent. The increase or diminution of the proportion of water in the alcohol employed is ascertained from its specific gravity, which becomes, therefore, a measure of the aqueous contents of the starch operated upon. The test is carried out in the following way:—Starch is covered with double its weight of alcohol, having at the normal temperature a density of ·8339; the mixture is frequently shaken during an hour, and the alcohol then filtered off and its specific gravity determined. For simplification the alcohol may be measured instead of weighed. For every 100 c.c. of alcohol (= 83·39 grams) 41·7 grams of starch must then be weighed off. The change effected in the specific gravity of alcohol by the different starch hydrates has been exactly determined by a number of experiments, and the following table has been constructed in which the resulting specific gravity of the alcohol is given, together with the corresponding percentage of water in starch:

Aqueous contents of Starch per cent.	Specific gravity of Alcohol	Aqueous contents of Starch per cent.	Specific gravity of Alcohol	Aqueous contents of Starch per cent.	Specific gravity of Alcohol
0	0·8226	22	0·8455	44	0·8643
1	0·8234	23	0·8465	45	0·8651
2	0·8243	24	0·8474	46	0·8657
3	0·8253	25	0·8484	47	0·8665
4	0·8262	26	0·8493	48	0·8673
5	0·8271	27	0·8502	49	0·8680
6	0·8281	28	0·8511	50	0·8688
7	0·8291	29	0·8520	51	0·8695
8	0·8300	30	0·8529	52	0·8703
9	0·8311	31	0·8538	53	0·8710
10	0·8323	32	0·8547	54	0·8716
11	0·8335	33	0·8555	55	0·8723
12	0·8346	34	0·8563	56	0·8731
13	0·8358	35	0·8571	57	0·8738
14	0·8370	36	0·8579	58	0·8745
15	0·8382	37	0·8587	59	0·8753
16	0·8394	38	0·8595	60	0·8760
17	0·8405	39	0·8603	61	0·8762
18	0·8416	40	0·8612	62	0·8775
19	0·8426	41	0·8620	63	0·8783
20	0·8436	42	0·8627	64	0·8791
21	0·8446	43	0·8635	65	0·8798

Perfectly anhydrous starch may be heated to 160° without undergoing any change: at a temperature of 200° it assumes a brownish-yellow colour, and is converted without any alteration in weight into a substance having the same composition and called dextrin, which is soluble in cold water. Starch containing about 18 or 20 per cent. of water is converted into dextrin at a temperature of 160°, especially if the heating be effected in closed vessels, so as to prevent evaporation of the water.

When starch is boiled with 200 times its weight of water it swells up to such an extent that it is apparently dissolved, and the liquid so obtained passes almost clear through a filter. This is due, however, less to actual solution than to an extraordinary expansion, as the apparently dissolved starch is again deposited from the liquid in a flocculent form upon alternately freezing and thawing the filtrate. In like manner the separation of water from apparently dissolved starch can be effected by bringing the roots of growing plants into the liquid; the plants take up only the water, the starch accumulating in flocks about the roots.

A mixture of starch with 12 to 15 parts of water may be heated to 55° without any change being effected in the starch; at a temperature of 57° the youngest granules begin to swell up, and in proportion as the heat increases the remaining granules

likewise swell up. At a temperature of 72° the liquid first becomes viscous, and when at the boiling point it is converted into paste.

The starch granules in swelling up may expand to twenty-five times their volume, and upon this depends the consistency of paste, which is thicker the less space the starch granules have in the liquid for expansion; the granules press against one another and form eventually an adherent shapeless mass. Upon cooling, the paste contracts and becomes harder, and when very thick it cracks. This contraction reaches its maximum when the paste is frozen, a separation of the water and starch taking place by the water crystallising out. Upon melting the frozen paste the water and starch do not again combine, but the water drains away, and the disorganised starch remains as a kind of felty mass, which when dry has the appearance of mother-of-pearl.

Solutions of potash or soda change starch into paste, even in the cold; treated with a solution containing 2 per cent. of caustic soda, potato starch swells to 75 times its original volume. This property is taken advantage of in testing flour.

Ammonia does not convert starch into paste. If a trace of starch be added to a solution of salt of ammonia and then solution of caustic soda drop by drop, the starch remains unchanged until the whole of the ammonia salt has been decomposed; but the least excess of soda causes immediately an expansion of the starch granules. The dilatation of starch in the cold is also caused by several acids in the diluted state, such as sulphuric, hydrochloric, nitric, and others. Concentrated solutions of various salts have a similar effect upon starch; thus, cold saturated or half saturated solutions of potassium bromide or sodium bromide convert starch into paste, but other salts, such as potassium chloride, have no such effect upon it.

The further action of acids upon starch differs widely according to the concentration of the acid and the temperature. When starch is heated to boiling with very dilute acids (1 to 2 per cent.), no formation of paste takes place; after a short time a complete solution is formed, containing at first a modified soluble starch, which passes into dextrin, and this is converted gradually into grape sugar, so that eventually the whole of the starch is changed into this form of sugar.

The same change as is produced by dilute acids at a high temperature is also effected by a number of other substances, the exact nature of which, however, is not known. Thus it is brought about by a substance called diastase, which is formed during the germination of cereals; also by a peculiar body found in the saliva and gastric juice of animals. The saliva and the gastric juice by their action upon starch render it digestible. The action of diastase is applied industrially in brandy distillation and in brewing.

Starch triturated with concentrated sulphuric acid is changed into starch sulphuric acid, a mucilaginous substance soluble in water. Upon neutralising the aqueous solution with bases uncrystallisable salts are formed. When the mixture of starch and sulphuric acid is diluted with alcohol it is decomposed, and deposits a greasy mass, which may be kneaded. If this be treated with water the greater part is dissolved, and upon filtering and adding alcohol to the clear filtrate white flocks are deposited, which are soluble in cold water but insoluble in alcohol. This flocculent substance is a modification of starch, having the same composition as starch, but differing from it by being soluble in cold water and not forming a paste. This soluble starch is formed under different conditions, as by the action in the cold upon starch of very concentrated or glacial acetic acid, and during the change effected in starch by dilute acids, etc. The fact, that when starch is triturated for a long time with a small quantity of water a small quantity of the starch passes into solution, is possibly due to the formation of this soluble modification through the heat generated by the friction.

Concentrated nitric acid (sp. gr. 1·52) dissolves starch even in the cold. Upon diluting such a solution with water a white powder is precipitated, which when dry explodes upon being struck. This substance is called xyloidin, and has the same composition as the corresponding compound of cellulose. Very dilute nitric acid behaves with starch in the same way as other acids. When starch is boiled with moderately concentrated nitric acid it is converted completely into oxalic acid.

Iodine in solution in water, potassium iodide, or dilute alcohol, when brought into contact with unchanged starch, starch paste, or soluble starch, immediately colours it blue, the coloration produced varying from light blue to almost black, according to the proportions between the starch and iodine. Solution of iodine in absolute alcohol does not produce the blue colour with starch, but the colour is immediately produced upon the addition of water. This reaction serves for the detection of starch and for distinguishing it from other substances, especially in microscopical researches.

Liquids containing only a very small quantity of starch (1 per cent.) are coloured blue by the addition of iodine, the starch iodide appearing to be completely dissolved; but upon dissolving salts in such liquids insoluble starch iodide is precipitated as the concentration increases.

Starch iodide suspended in water is bleached by the sunlight, owing to the conversion of the iodine into hydriodic acid; but the colour is restored by ozone and other oxidising agents. All alkalies by combination with the iodine of starch iodide, decolorise it, but the addition of acids causes the colour to reappear.

Starch iodide suspended in water loses its colour also when heated to 66°, the coloration reappearing upon cooling. This experiment may be performed with the same portion of starch iodide several times, but the blue colour gradually disappears, owing to the volatilisation of the iodine; the addition of a fresh quantity of iodine immediately restores the colour.

The reaction between iodine and starch only takes place when both are present in the free state; thus, potassium iodide gives no coloration with starch. The characteristic blue colour appears in this case only when some of the iodine in the potassium iodide has been set free by such reagents as chlorine, ozone, nitrous acid, etc.; iodine is not liberated in the free state by hydrochloric, sulphuric, and nitric acids, but converted into hydriodic acid. A mixture of potassium iodide and starch is therefore a useful reagent for the detection of chlorine, ozone, peroxide of hydrogen, nitrous acid, etc.

The different behaviour of starch, dextrin, and sugar towards iodine makes it possible to follow the changes effected in starch by dilute acids, diastase, saliva, etc. So long as unchanged or modified starch is present the addition of iodine produces a blue coloration; when the starch is almost completely changed into dextrin, a characteristic red colour appears; finally, when nothing but sugar is present, no colour at all is produced by iodine. This test requires that the liquids should be cold, on account of the decoloration of starch iodide at a slightly-elevated temperature.

Starch possesses the property of combining with bases. Upon mixing together a solution of caustic soda (6 parts soda to 200 parts water) and water containing starch suspended in it (25 parts starch to 100 parts water), a transparent colourless jelly is formed after a short time, which is a compound of sodium hydrate and starch. If this jelly is mixed with a 7 per cent. aqueous solution of calcium chloride a double decomposition takes place, and a thick white insoluble mass is formed which is a compound of starch with lime, sodium chloride being in solution. A series of compounds of starch with other bases may be similarly formed in which the starch cannot be detected by means of iodine. The starch in such compounds is immediately set free upon the addition of acids.

Starch exhibits a characteristic reaction with ammoniacal copper solution (Schweitzer's cellulose test). If 40 times its volume of ammonium cuprate be poured over starch and allowed to stand six hours, the starch swells up to ten times its original volume; examined under the microscope the granules appear translucent and of a bluish colour. The substance when washed with ammonia gives up copper oxide, and, if the washing be continued until the entire quantity of copper oxide is dissolved out, the residual starch likewise dissolves in aqueous ammonia. Starch is by this process converted into its soluble modification. If water be used for removing the excess of copper solution the starch dissolves, and a greenish compound remains behind, being a compound of starch with from 12 to 13 per cent. of copper oxide. This compound may also be obtained direct by pouring very thin starch paste into an ammoniacal copper solution.

When this compound is treated with hydrochloric acid it is immediately decomposed, and, according to the amount of water present, is either converted into a jelly or is completely dissolved. The addition of alcohol to the jelly or the solution causes the separation of the starch, which then gives a blue colour with iodine. No conversion of starch into dextrin is effected by this treatment.

All the substances belonging to the starch group are closely related to sugar. Thus, every kind of starch when boiled or heated under pressure with dilute sulphuric acid, undergoes alteration and is converted into a substance known as dextrin, having the same composition as starch, but like the substance occurring in British gum (see p. 800), being very soluble in water and causing the rotation of a polarised ray from left to right; if the boiling or heating be continued, dextrose sugar is formed by the fixation of a molecule of water. It was formerly supposed that, by the action of dilute acids, starch is converted wholly into dextrin by mere alteration of its physical structure, and that by continuing the treatment dextrin combines with the elements of water, giving rise to the formation of glucose. But recent experiments by Musculus appear to indicate that both dextrin and glucose are produced simultaneously by the action of dilute acids upon starch, and that the substances thus produced bear the proportion of 1 molecule of glucose to 2 molecules of dextrin, according to which result, the molecule of starch may be regarded as having a composition represented by the formula $C_{18}H_{30}O_{15}$, and its decomposition by dilute acids may be represented by the following equation:

$$C_{18}H_{30}O_{15} + H_2O = C_6H_{12}O_6 + 2C_6H_{10}O_5.$$

Again, during germination the diastase of seeds converts starch into a soluble mixture of dextrin and dextrose, or maltose (see p. 803) in various proportions, according to the temperature and other conditions under which the action takes place. Although starch cannot be induced to undergo fermentation by means of yeast, yet Berthelot has shown that chalk and cheese at 38° C. cause the fermentation of starch, with the production of a considerable amount of alcohol; doubtless sugar is produced as an intermediate principle. Starch, like sugar, also yields oxalic acid on oxidation with nitric acid.

Inulin ($C_6H_{10}O_5$) is found in quantity in the roots of *Inula Helenium*, *Helianthus tuberosus*, and *Dahlia*, and may be prepared by merely rasping them and levigating with water; inulin deposits from the washings, on standing, and may be readily purified by solution in hot water and precipitation by alcohol. It is a white amorphous tasteless substance, nearly insoluble in cold water, but freely soluble in hot water. Iodine produces a brown coloration. It has the same percentage composition as ordinary starch, and when boiled with dilute acids is completely converted into lævulose.

Glycogen is the name given to a kind of starch or amylaceous principle produced by the livers of most animals, and it is supposed to constitute the intermediate product in the formation of sugar in the animal organism. It is a white amorphous substance, without taste or smell, insoluble in alcohol, and yielding with water an opalescent solution. When boiled with dilute acids it is converted into glucose.

No kind of starch exists as such in the brain, notwithstanding the numerous statements which have been made to this effect. The reactions, which have probably led to this statement being made, are referable to a substance named cerebrine, and to others allied to it, all of which yield dextrose on boiling or heating under pressure with dilute sulphuric acid. This reaction would indicate the existence in these substances of a starch-like molecule, in spite of their nitrogenous nature.

In the chapter on Cellulose (see p. 615) it will be seen how very much its properties assimilate to starch, and indeed it has a like composition. That there is a very distinct difference between the various members of the starch group is shown by many facts, notably because inulin for instance yields lævulose, whilst ordinary starch yields dextrose on boiling with dilute acids.

As a whole, the starches seem to be constituted on the type of a complex ether, under which light the sugars may be regarded as polyatomic alcohols derived from them; but the true constitution of no one kind of starch or sugar has so far been determined.

The alcoholic nature of sugar derives considerable support from the researches of Berthelot, who has shown that when fatty acids and various sorts of sugar are heated together under certain conditions, water is eliminated, and saccharides are formed which on boiling with dilute acids yield again sugar and fatty acids.

Starch is known to form a colligated acid with strong sulphuric acid, and recently Kingzett and Hake have shown that certain kinds of sugar and various benzene derivatives may enter into coloured combinations under the influence of strong sulphuric acid—possibly by the abstraction of water. Such compounds have several characters in common with the better known and simple combinations of the alcohols with sulphuric acid. (See Ethers.)

Preparation.—The method of extracting starch from the amylaceous parts of plants consists in reducing the material to pulp, either by grinding or rasping and mixing with water, then washing the pulp with a stream of water so as to float the starch granules away from the disintegrated cellular tissue.

The materials from which starch is chiefly prepared are potatoes, wheat, rice, maize, and the grain of other cereals. Several other varieties of starch, commonly known as arrow-root, are obtained from the tubers of *Maranta arundinacea*, etc.

Manufacture of Starch from Potatoes.—This includes the following operations: Steeping, washing, separation of stones, rasping, straining, settling, removal of the starch, purification, second straining, washing, draining, and drying in the air or in a centrifugal machine, drying in an oven, packing.

Steeping.—Potatoes grown in tough clay or loam are covered with adherent earth, etc., which clings so tenaciously as not to be removed by simple washing. They are therefore allowed to soak for several hours in a large vat containing water.

Washing.—In the washing an apparatus called the washing drum is used, consisting of a hollow revolving cylinder, the case of which is formed of wood or iron bands ½ to 1½ inch broad, and fastened at intervals of about ¾ of an inch. The cylinder is slightly inclined, and dips to half of its diameter in water placed in a capacious vat. It makes about fifteen revolutions per minute, by which means the

potatoes are kept in continual motion, rubbing against and being rubbed by the case of the cylinder. The heavier portion, the sand and small stones, sink to the bottom and fall through the intervals between the bands. The potatoes are introduced at the upper end of the cylinder, and by the action of a spiral arrangement revolving on its axis are thrown out at the opposite end; where, falling upon the edge of the vat, they roll along a sloping latticed surface to the stone catcher.

Payen proposes a more energetic purification by the use of a large circular brush, with a revolving cylinder also furnished with brushes, the interval between the central brush and those of cylinder being only sufficient to allow of the passage of a medium-sized potato. The larger and smaller potatoes being previously separated, are to be washed in a specially wider or narrower cylinder. A sufficient rigidity could be given to the brushes to remove at the same time the epidermis and the substances adhering to it, and so obtain a material free from skin. On the other hand, the great wear and cost of renewing the brushes must be considered.

Separation of the Stones.—In the French manufactories this is effected by the stone catcher of Joly (fig. 534). This apparatus consists of a semi-cylindrical

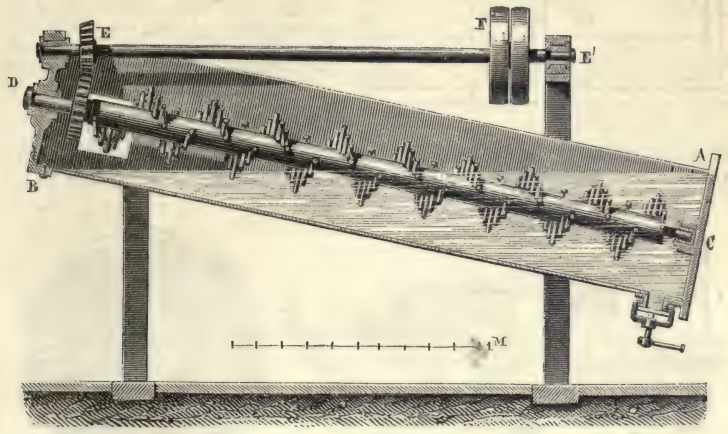


Fig. 534.

sloping trough, filled with water to the level A B In the trough is a shaft (C D) furnished with arms placed spirally, which, through the cogwheel, is rotated by the driving wheel (F). The shape of the arms is shown by figs. 535 and 536. The potatoes being thrown in at A, are rubbed upon one another by the arms and repeatedly dipped in the water, so that the remainder of the dirt and all stones and sand is washed off, and the heavier particles sinking to the bottom are removed from time to time through an opening. The potatoes are carried forward by the action of the spiral until they reach the upper end of the trough, over which they fall into the hopper of the rasping machine.

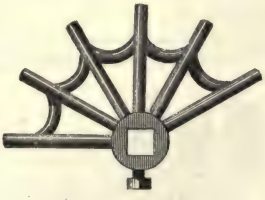


Fig. 535.



Fig. 536.

It appears to be preferable to remove the stones and the greater part of the sand by the first washing, as is done in the German factories. With this object the vat in which the washing drum is placed is separated into two unequal divisions, the larger for the washing drum and the smaller for the stone catcher. The potatoes are placed in the water in the smaller division, and are drawn forward and kept in incessant motion by six or eight large arms arranged spirally on a prolongation of the shaft of the washing drum. The potatoes thus reach the washing drum previously washed and freed from stones.

Too much care cannot be taken in the complete removal of all stones, as these would have a most injurious effect upon the machinery used in the subsequent operations.

Rasping.—The rasper, represented by figs. 537 and 538, consists of a cylinder (*a a*) armed with steel saw blades, which are fastened by iron bands at intervals of about $\frac{1}{2}$ an inch, and project about $\frac{1}{8}$ an inch from the cylinder. The washed potatoes are passed into the machine through the spout (*b b*), and being seized by the cylinder—making 800 revolutions per minute — are pressed against the casing enclosing it; the teeth of the saw blades tear through the potatoes and reduce them to pulp, which falls through the hopper (*d*).

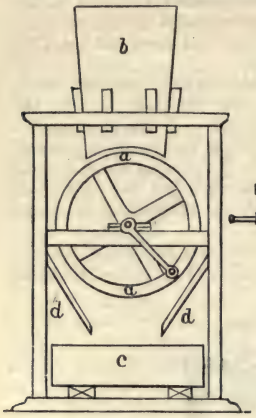


Fig. 537.

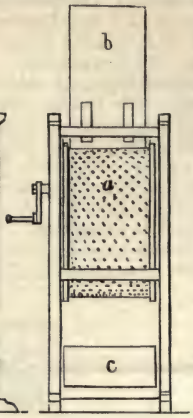


Fig. 538.

The rasper has been altered and improved by Champonnois, and in its modified form yields a more uniform and finer paste. This consequently admits of a larger product being obtained, since it is only the starch from the cells actually ruptured that can be obtained, whilst all that remains in closed cells is lost to the manufacturer.

Champonnois' rasper, which is represented by figs. 539 to 542, like the other, consists of a cylinder furnished with saw blades; but the essential peculiarity is, that instead of the blades being on the

Fig. 539.

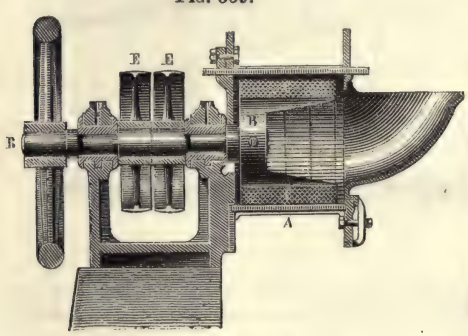


Fig. 540.

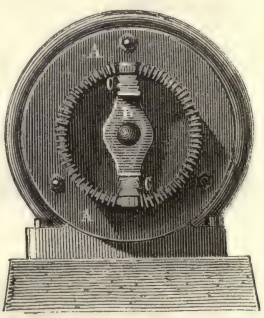




Fig. 541.



Fig. 542.

surface of a solid cylinder, they are arranged on the inner surface of a hollow cylinder, and instead of the cylinder rasping against the potatoes, the potatoes are rubbed against the cylinder. The case of the cylinder is shown in fig. 540 (A), with the peculiar rasper inside. The rasper is so arranged that from one to four saw blades lie between thin steel bands, and between each group is a space through which the paste formed can flow. In the machines first constructed there was an interval of $\frac{1}{16}$th of an inch between each saw blade, but in those of recent construction there is an interval between each four saw blades which is reduced to from $\frac{1}{50}$th to $\frac{1}{25}$th of an inch; by this arrangement a finer paste is produced and the probability of clogging diminished. Figs. 541 and 542 show the arrangement with an interval between every blade. In the axis of the rasping cylinder is a shaft (B B) making 800 to 1,000 revolutions per minute, by power applied to the wheels (E E) and regulated by a fly wheel; at the other end of the shaft within

the drum is a strong fork-shaped scoop. The potatoes falling through a side opening are seized by the scoop and pressed forcibly against the saw blades in the cylinder (c). Water being admitted into the interior is driven by centrifugal force against the sides of the cylinder, and makes its way through the interstices, carrying with it the potato paste formed, which passes away through a pipe underneath. The teeth of the saw blades are very short, projecting $\frac{1}{5}$th of an inch from the drum. They require reversing twice a day, and after two days' use need to be refiled. As much as 13 tons of potatoes can be rasped by this machine in ten working hours, whilst the yield of starch from a given quantity of potatoes is considerably increased.

Straining.—The paste thus obtained is a mixture of starch and potato fibre. To separate them the paste is washed with water upon brass-wire sieves of different degrees of fineness, which allow the starch granules to pass through with the liquid, and retain the coarser portions of the fibre. The pulp is made to pass over the sieves by means of an endless band, and various arrangements are in use for this purpose.

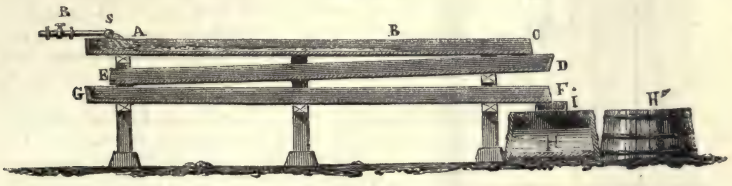
As the washed pulp always retains a portion of the starch, and more in proportion as the rasping is imperfectly performed, different plans have been proposed for its recovery. Huck subjects the pulp to a second rasping, but the benefit from this is very doubtful. Fiska passes the pulp between two cylinders, one revolving more rapidly than the other. The membranes of cells that escape the action of the grater are in this way ruptured, and as much as 3 per cent. more starch is thus set free.

Settling.—The starch liquid as it comes from the sieves generally contains some sand which was not separated during the washing of the potatoes and was too fine to be retained by the sieves. It is therefore run into a large vat and vigorously stirred so as to bring all the starch into suspension. Before the starch has had time to settle, but after the sand through its greater specific gravity has fallen to the bottom, the liquid is run off by means of a wide syphon, or through a cock placed near the bottom of the vat, into another capacious vat, where it is allowed to stand for four hours, by which time the starch settles to the bottom. The supernatant liquid containing the sap constituents of the potato is then removed.

Purification.—The lower part of the sediment deposited in the vats consists of pure starch, but this is covered by a greyish layer consisting of fine fibres that have passed through the sieves. This impure mass is scraped off with a special instrument and undergoes another operation to remove from it the starch it contains.

The purified starch is again suspended in water by the action of a stirrer, then passed through a silk or wire strainer (90 meshes to the inch) and again allowed to settle. The starch is then placed in a slightly sloping flat-sided trough (figs. 543 and 544, A B C), about 22 feet long, 3 feet wide. Below this is a second trough (D E), in-

FIG. 543.



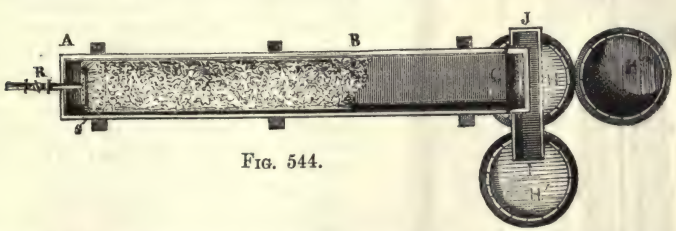


FIG. 544.

clined in the contrary direction, and a third (G F) inclined like the first. A spray of water from a very fine rose (S) controlled by a cock (R), falls upon the starch which is placed beneath it, and at the same time stirred with a spatula. The water gradually washes all forward with it, but while flowing slowly along the troughs, the starch is deposited and only the lighter fibrous matter remains suspended and passes with very little starch through the gutter (J J, fig. 544) into the vats (H H′ H″). The starch deposited is added to that purified in the first settling vat and is then ready for draining.

The residual washed pulp is generally used as fodder, either in the fresh condition, when it has had a portion of its water removed by pressure, or after it has undergone fermentation in pits. The pressure is applied by passing it through a pair of cylinders between two endless bands of cloth, by which half the water is removed. When not used in the fresh state it is stamped into pits, covered with straw, and then with a layer of earth. It there undergoes acetic fermentation, by which, however, its food value is not deteriorated. When using the pulp as fodder it must be borne in mind that it consists almost exclusively of non-nitrogenous materials, and that it is necessary to supply albuminoid constituents by the addition of oil cake, bran, etc.

When dried the pulp is easily ground to powder, and in this form is sometimes added to wheaten-flour in bread-making. But this can scarcely be done profitably, as it is very questionable whether cellulose, which is easily digested by beasts, is digestible by man, especially after being dried. But it can be used in the place of flour for dusting the hearth of the oven to prevent the paste adhering. Lastly, the pulp is also used in the glucose, beer and brandy manufacture.

The moist but drained pulp contains about 12 per cent. of solids, about 7 per cent. of which is starch, a proportion however which is correspondingly lessened by the arrangement for crushing and good rasping.

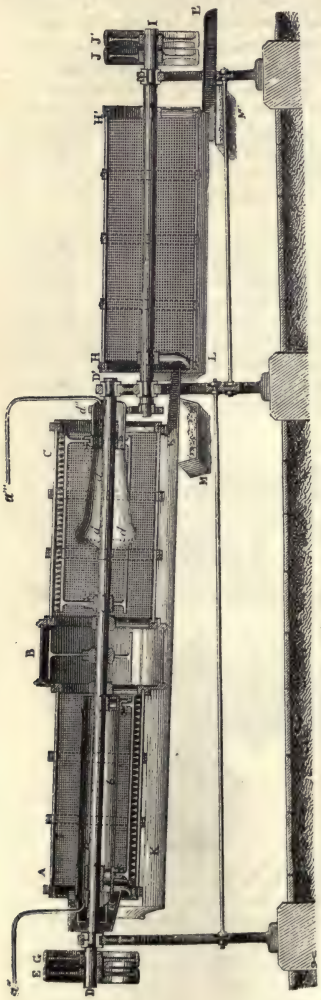


FIG. 545.

Several other forms of apparatus have been constructed for carrying out these operations, especially for washing and straining. A longitudinal section, of that of Huck and Stoltz, is shown in fig. 545. It consists of three cylinders, the case of the first (A) being formed of a wire sieve, 25 meshes to the inch. The paste from the rasper is introduced through the funnel (*a*). Within this cylinder is another formed of perforated metal plate into which water flows through the pipe (*a''*), and is distributed uniformly through the perforations upon the potato pulp in A. This gradually moves forward, and comes, after parting with the greater part of its starch, into the second cylinder (B), which is covered with sheet copper. The pulp is here agitated with a fresh jet of water, coming through the perforated pipe (*d*) supplied from *a'''*, and carried forward into the third cylinder (C) covered with wire tissue, 35 meshes to the inch. Whilst in the cylinders the paste undergoes a continual working, in A and C with brushes and in B with a T-shaped iron, both fastened to the shaft (D D'), which is rotated by the driving-wheel (G) in an opposite direction to the cylinder. The liquid flowing from A and C collects in the trough (K) below and from thence runs into another sieve cylinder (H H') covered with wire gauze, 50 meshes to the inch. The fibrous pulp which has passed through the other sieves is here retained, the liquid then running off along the trough (L) into the settling vats. The coarse pulp is pushed out of the cylinders and falls into the receivers (M M') underneath.

In order to prevent the clogging of the sieves a fine stream of water is thrown upon them during revolution from pipes running parallel with their axis.

In most manufactories the wash water is allowed to flow into the nearest ditch or watercourse. It contains all the soluble constituents of the potato, including nearly all the albumin and other substances that are highly putrescible and these

afford favourable conditions for the development of numerous algæ, oscillaria, beggiotoa, vibrios, etc. These increase so rapidly that frequently in a short time the bed of the watercourse is filled with them. Many of the algæ have the property of decomposing sulphates dissolved in the water with evolution of sulphuretted hydrogen, contaminating the air and rendering the water unfit for man, beasts, or fishes. The waste water from sugar manufactories behaves similarly but in a higher degree. Many attempts have been made to remedy these inconveniences, which give rise to numerous actions against the manufacturers by the inhabitants and regulations by the government. Payen recommends that the water should be allowed to clear in several cisterns. In the first it deposits principally starch, and in the latter albuminous substances, after which the water itself may be used for irrigation. The deposit in the cisterns can be used as manure. The quantity of manure which can be utilised in this way during the operations of a three months' season is considerable, and Payen estimates that it is obtainable at one-fifth of its market value. If there is sufficient land in the neighbourhood of the manufactory, a system of direct irrigation is the best and simplest method, experience having shown that the effluent water is not injurious. When this is not the case, the disinfection of the water with a milk of lime to which magnesium chloride has been added is recommended. Part of the lime and magnesium forms with the different organic substances insoluble compounds which are mechanically carried down by the remainder, so that a comparatively pure water flows off from the first settling basin.

According to Fesca, a large proportion of the albuminous bodies can be recovered and used as food for cattle by boiling the fresh wash water, when the albumen is coagulated and deposits as a flocculent mass.

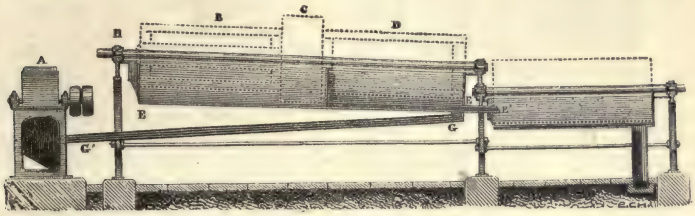


Fig. 546.

Figs. 546, 547, and 548 show a modification by which considerably less water is required. The paste coming from the rasper (A, fig. 548, enlarged) is raised by the centrifugal pump (D) into the first cylinder (B, fig. 546), where it gives up by far the greater part of its starch. The strained liquor from this cylinder is not joined with that from the other cylinders, but run off into the purification vessel. The liquor from the mixing cylinder (C) and the other



Fig. 547.

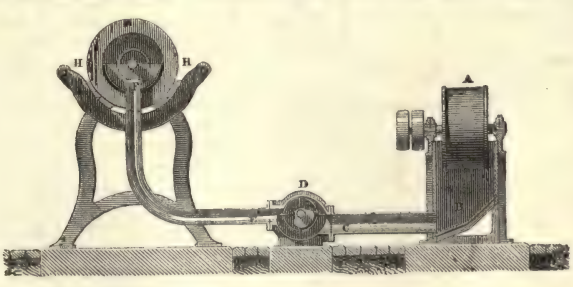


Fig. 548.

sieve cylinder (D) which contains but little starch is carried by the pipe (G G') back to the rasper, where it is used for the first thinning of the paste.

By the further modifications shown in fig. 549 a second working of the pulp is effected and a larger yield of pulp secured. The pulp thinned with water falls from the rasper driven by the wheel (A) into a small cistern, from which it is raised by the pump (B) through the pipe (B′) into the sieve and mixing cylinders (D D′ D″), and in the latter washed by a stream of water (*a*′). The pulp rejected from D″ falls into the hopper of a second rasper, where it is rubbed between two cylinders (F) rotating in different directions. It then flows into the sieve (G), where it meets with more water from A″ and A‴, and being washed falls into a trough, along which it is pushed by an archimedean screw. The starch liquid from D falls into the trough (E), that from G into E′, and both united flow into the first purifier (K L); the purified product flows through the trough (J) into the cistern (M), from whence it is raised by the pump (N) to the second purification apparatus (O), where the last portions of fibre are left, and the liquid passes through the trough (P P) to the settling vats or the inclined plane, by which in the larger factories the settling vats are now completely supplanted. For the working of twenty tons of potatoes per day a trough is required about 90 yards long and 3½ feet wide, with a fall of 1 to 1½ per 1,000 (see fig. 550).

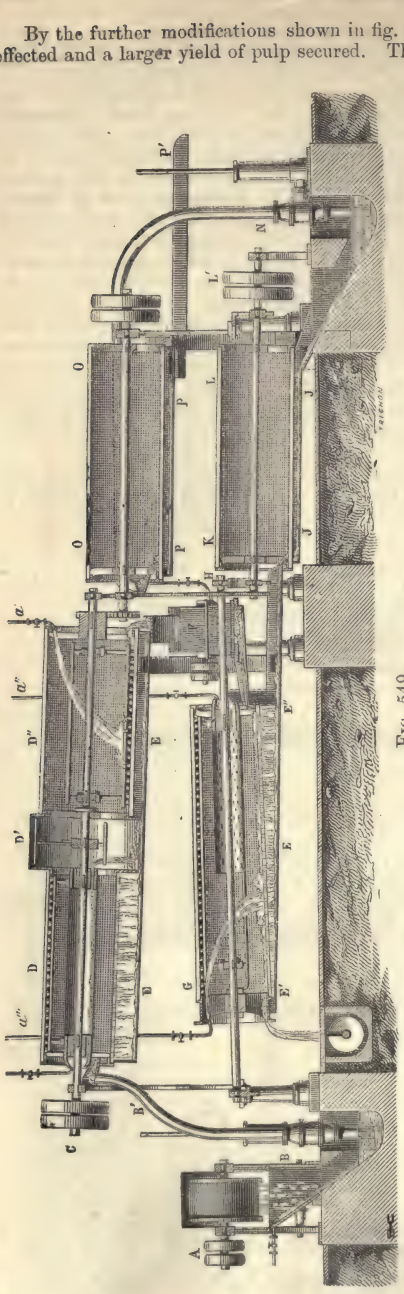


Fig. 549.

The starch from the troughs is sufficiently pure to be sent at once into the market; but as it is still contaminated by the potato sap, it is advisable again to wash it with water in the settling vats. When the inclined plane has been used this last purification is much more easy, the greater part of the impurity having been already separated.

Drying.—The starch is left behind in the settling vats as a very thick paste, from which the water is removed by centrifugal action, by drying in the air or in ovens.

In drying starch by centrifugal action the same apparatus is used as in draining the syrup from the raw sugar crystals in the sugar manufacture (see Sugar). It needs now only to be mentioned that it consists of a shallow cylindrical drum, the case of which is made of wire gauze. The drum being very rapidly rotated, the water is forced out by centrifugal force, whilst the starch is retained by the wire gauze. The starch as it comes from the settling vats or the inclined plane is unfitted for the centrifugal machine, being too thick to become so equally distributed as is necessary to the proper working of the machine. It is therefore stirred with sufficient water to bring it to the condition of a liquid paste that will flow into the apparatus while it is in motion, when it is immediately

flung against the circumference, the water flies off, and the starch lies as a compact round cake upon the case of the cylinder.

A fresh process of purification may easily be combined with the use of the centri-

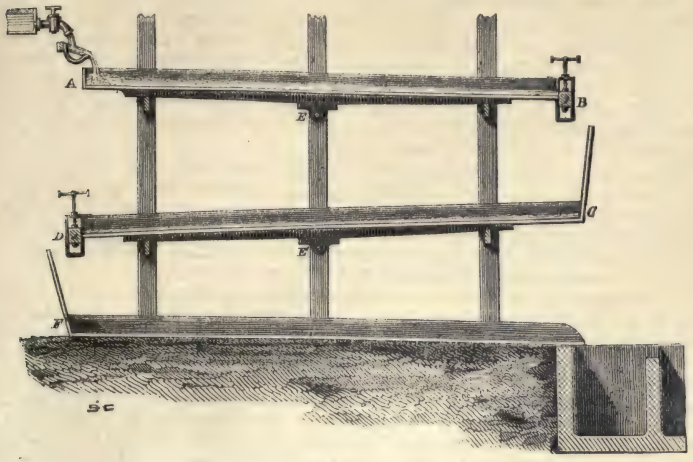


FIG. 550.

fugal machine. The densest and most heavy portion is driven off most rapidly and furthest by the centrifugal force, the lighter portion less rapidly; the largest and purest granules therefore lie closest to the sieve. The fibrous portion remains longer suspended, and is at length deposited as a layer upon the surface of the pure starch, from which it is easily removed. A suitable purifying centrifugal machine has been constructed by Fesca of Berlin.

For different purposes, such as the manufacture of dextrin and starch sugar, the starch as it comes from the centrifugal machine is perfectly suitable. It contains 35 to 40 per cent. of water, and is known in commerce as green starch.

Where a centrifugal machine is not used the water is removed as much as possible from the starch before proceeding with the drying. The paste is therefore laid in shallow receptacles made of clean smooth slate slabs, then covered with clean linen cloths, and on the top are laid dried porous stones. The stones absorb the moisture, and after a short time green starch remains. This is next removed to the drying floor, where it remains freely exposed to the air until sufficiently dried. During this time, which varies in length with the period of the year, the starch is exposed to many accidents, especially to becoming dusty. This should be considered in the construction of the drying floor, which should be as far removed as possible from dusty places. Another disadvantage is the freezing of the moist starch, as paste made from once frozen starch is, in the opinion of experts, deficient in cohesive power.

Both these defects may be avoided by drying the starch in ovens. According to this method, a current of warm air is circulated through closed chambers, and a methodical evaporation of the water is thus effected. The temperature is so regulated that the green starch is heated to 60°, not too rapidly or beyond, otherwise the starch swells and becomes pasty; but when the greater part of the water has been removed, the temperature can be raised considerably.

During the drying of potato starch, the larger proportion of it crumbles spontaneously to powder; differing in this respect from wheat starch, the granules of which remain pressed together. The powder is sifted, the retained firmer granules passed under a roller, and the whole then well mixed. The dried starch is now ready, and is packed in paper-lined vessels and sent to market.

MANUFACTURE OF WHEAT STARCH.—The process of obtaining starch from wheat is somewhat different from that before described for its manufacture from potatoes. Whilst the potatoes are only treated so as to rupture the separate cells in order that the starch stored up in the sap may be washed out, in the case of wheat a separation has to be effected of the starch from the surrounding gluten and the removal of the husk and remaining constituents of the grain. This can be carried out by two essentially different methods.

(1.) By utilising the plastic property of the gluten, which allows the starch to be washed out from the dough, the pure gluten remaining.

(2.) By destroying the gluten through a process of fermentation and decay, by which a part is rendered soluble and a part loses its coherence, and can then be separated from the unaltered starch.

The latter method has long been used, and at the present day it is met with in by far the greater number of manufactories. But it has many inconveniences: a large quantity of gluten, which could be used as fodder or as human food, is lost; the yield of starch does not correspond to the amount in the grain; the waste discharge from the manufactory, laden with putrefying and fermenting material, is dangerous to the health of the neighbourhood, spoiling the water in the streams into which it flows and diffusing a most disgusting smell.

Production of Starch and Gluten from Wheat Flour.—According to this method, introduced by Martin, a dough is first prepared, exactly as for bread making, 100 parts of flour and 40 to 50 parts of water being mixed together. The dough is kneaded, either by hand labour or in a machine, until perfectly uniform, and then, in order to allow the dough to become saturated with moisture before washing, it is allowed to stand in summer 25 minutes and in winter one hour.

For the washing out of the starch a semi-cylindrical trough is used, at different parts of the circumference of which are slits covered with wire-gauze, to allow of the discharge of the water holding the starch in suspension. At the bottom of the trough is a slightly channelled cylinder, to which a mechanical arrangement imparts a swinging motion to and fro. The dough, formed into small balls, is placed in the trough, and whilst a fine jet of water plays upon it incessantly from a water pipe, it is continually moved to and fro by the cylinder. The starch is thus washed free, and flows together with the water through the openings covered with wire to the receiver; whilst the gluten gradually becoming more compacted together, is left finally as a tenacious elastic mass, possessing the characteristic properties of that substance. In such an apparatus, with a trough 6½ feet long and 4 feet wide, the dough from 2 cwt. of flour can be worked hourly with an expenditure of about 100 gallons of water.

In apparatus of more recent construction two washing troughs are placed next to each other, the working power being thus doubled. Fig. 551 shows a section of the

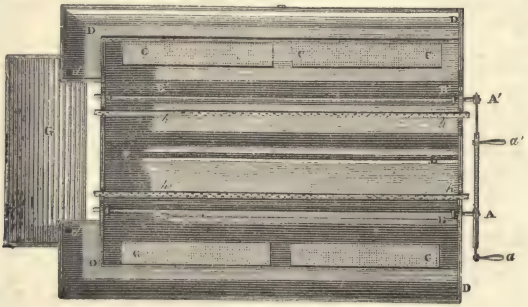


Fig. 551.



Fig. 552.

apparatus; fig. 552 gives a view from above; and fig. 553 an end view. The letters designate the same parts in each. FF are the wooden troughs. In fig. 553 at C is shown one of the openings covered with wire-gauze. The longer sides are provided with two wide gutters (D D), in which, by means of a movable outflow arrangement,

the liquid is so retained that in both the gutters and the trough it reaches to half the height of the wire-gauze, the excess of starch-laden water flowing off, through a pipe (*d*, fig. 551) that can be raised or lowered at pleasure, into the receiver (G). Over the partition common to the two troughs is placed an arched plate for the purpose of breaking the waves of the liquor when set in motion and preventing it from running from one trough into the other. A A′ are two iron shafts resting in sockets on the sides of the trough. At each end of these shafts are iron arms having forked extremities which span the ends of the corrugated wooden cylinders (B B′), so that the latter can turn freely in the fork. By means of the handles (*a a*) connected with the shaft (A A′) an oscillatory movement is imparted to the cylinders (B B′) at the bottom of the trough. At first the turning of the handle requires the exercise of considerable force, but after about ten minutes the volume of the dough is much reduced, and the work becomes lighter. The water is brought to both troughs through copper pipes pierced with fine holes, through which it falls during the whole operation in fine jets upon the moving dough underneath.

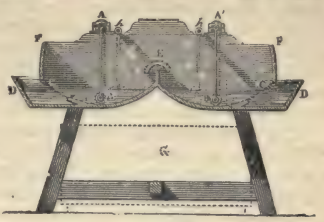


Fig. 553.

The operation with this apparatus is carried out in the following manner. A sack of flour is made into dough with about half its weight of water, which requires in summer 20 to 30 minutes or in winter an hour. This dough is worked into balls of about two pounds in weight, and distributed equally in both troughs, where being partly covered with water it is rolled to and fro by the cylinders. If the dough becomes adherent in larger lumps, it is at once again divided up by the workman in charge. Care has also to be taken that the wire-gauze does not become stopped up by small pieces of gluten; this is prevented by applying with one hand a brush to the outside whilst the portions of gluten are removed from the inside by the other. The washing of the dough lasts about an hour, after which time the water scarcely carries off any more starch. The outlet pipe (*d*) is then entirely withdrawn from the gutter (D), which allows the fluid contents of the gutter and trough to flow away into the receiver (G). The gluten which is left behind is freed from excess of water by five minutes' kneading and removed, and the apparatus is then ready for a fresh operation.

On the average there is obtained from a sack of flour about 110 lbs. of moist gluten and a liquid containing equal to about 220 lbs. of dry starch. The most suitable kinds of wheat for this method of manufacture are the half-soft wheats; neither from the hard horny nor from the soft mealy wheats is the production of starch and gluten to be effected with equal results.

Martin's method also allows of the use of bruised wheat. The operation is exactly the same as just described; though the products differ in so far that, with a pure starch, there is obtained a gluten mixed with corn husks, which cannot be used for human food, though suitable for fodder.

The purification of the starch is essentially the same as described under Potato Starch. Upon running off from the trough the liquor first passes through a fine wire sieve, 100 meshes to the inch, which retains some membrane and small particles of gluten carried off by the water. From the first receiver the liquor is raised by a pump to a higher reservoir, from which it flows on to the inclined surfaces described. The pure starch is deposited and soon forms a thick uniform layer, whilst the lighter and impure portion is carried forward to the end of the inclined surface, and finally collects in the reservoir underneath. There it is allowed to remain at rest for twenty-four hours, during which the starch settles at the bottom and the liquor becomes clear. This liquor contains more or less albuminous matter, dextrin, grape sugar, and salts, and can be used either as a drink for cattle and horses, or in the preparation of beer or brandy. After the separation of the clear liquor the impure starch obtained is subjected to a further purification by stirring it with water, passing it through a fine sieve, and then running it in a very thin layer upon the inclined surface. Pure starch is again deposited, whilst from the water flowing off there is a further settlement after standing forty-eight hours of a small quantity of very inferior starch, which is drained in a linen filter, pressed and dried.

By a still more recent method of Martin's, the impure starch can be readily freed from foreign admixture and a better product obtained than is possible through simple washing. It consists in treating the starch, after the first deposit has been collected upon the inclined surface, not simply with water, but also with a weak solution of caustic soda, by which the gluten is dissolved before the starch is attacked. After the

settling and removal of the supernatant liquor, the deposit is stirred with water and solution of caustic soda, specific gravity 1·013, added until the liquor blues red litmus paper. The liquor is allowed to act for two hours; then a considerable quantity of water is added, and the whole is thrown on a No. 200 sieve, which retains the swollen gluten and allows the starch to pass through. After standing a short time, during which a small quantity of sand settles, the starch milk is poured on to the inclined surface. Almost the whole of the starch is thus obtained as first product, whilst with simple washing about 25 per cent. is produced in an impure unmarketable form.

The pure starch deposited upon the inclined surface is once more stirred up with water, then passed through a fine sieve, and allowed to settle during twenty-four hours. After the removal of the supernatant liquor, some impurities are found in the top layer, which is removed and submitted to further operations.

In order to dry the starch it is first spread out evenly in a flat stone receptacle, covered with clean linen cloths, and overlaid with some porous material that will absorb moisture, such as burnt porous limestone, gypsum, purified ashes, etc. After a short time the starch loses so much water, that it can be cut up in the form of large blocks as green starch. These blocks are then dried upon hollow stands, situated in airy places. As the water evaporates from the surface of the mass, moisture is drawn from the interior, carrying with it a small quantity of impurities still present, and a fungoid growth commonly takes place on the yet moist surface, which causes the appearance of yellow spots. The impurities and vegetation give to the cake an unseemly appearance; as soon therefore as the drying is so far advanced that no further development of vegetable organisms is possible, the outer surface is carefully scraped off with a knife. This refuse is known as starch scrapings.

The purified cakes are broken up into smaller pieces, Schafchen, and perfectly dried, in summer in the open air, and in winter in heated rooms.

Wheaten starch differs essentially in its appearance from potato starch. Whilst the latter, upon drying, crumbles more or less into a fine powder, the granules of wheaten starch lie close together and assume a rod-like structure, so that a broken cake or the surface of a mass appears to consist of prisms lying nearly regularly one upon another.

Production of Starch by Decomposition of the Gluten.—In this process either whole or crushed grain is used, but whole corn is most frequently used. The wheat is placed with water in a large receptacle, and left in contact for about three days, or until it has become so uniformly penetrated by moisture and softened that, by moderate pressure between the fingers, the outer husk separates from the grain and the latter is crushed into a milky mealy mass. It is very advantageous to the quality of the product if a washing of the grain is effected, together with the soaking, in order to remove dust and adhering impurities. This can be done by changing the water every twenty-four hours until it remains clear and colourless.

The swelled corn is crushed either between two wooden cylinders revolving in opposite directions and fed through a hopper, or by one or two cylinders revolving upon a horizontal stone having a rim. The husks of the softened corn are thus easily separated.

After the crushing follows the fermentation. This is effected in large stone vessels, into which the swelled corn is passed direct from the crushing mill, and then stirred up with some water. In order to induce the fermentation, some liquor, or sour water, derived from a previous operation is added. During this fermentation various processes go on simultaneously. A constant evolution of gas takes place, resulting from alcoholic fermentation; the alcohol formed is converted by further fermentation into vinegar; besides these, lactic fermentation takes place, and other fermentations the products of which have not yet been studied. Actual putrefaction, understanding by this term the fermentative processes which evolve stinking gases, must be avoided; the fermenting mass should always have an agreeable vinous smell. The duration of the fermentative process differs with the temperature of the surrounding atmosphere; usually it has progressed sufficiently in three or four weeks. The liquor in which the pulpy mass is contained, the sour water, has then acquired a light yellow colour, and has a peculiar sticky feeling, the starch separates readily from the husk, whilst part of the gluten is dissolved and the other part is softened, and has completely lost its adherent elastic properties.

The separation of the starch from the fermented mass takes place in the washing wheel or washing drum. This consists of a shallow cylinder, which is rotated vertically by a shaft passing through it. The surface of the cylinder is either made of wooden staves pierced with fine holes or from perforated sheet copper. At the extremities are strong wooden covers, having an opening that can be closed, for the purpose of filling and emptying the cylinder. On one side water flows in through a pipe opening in the shaft. The lower half of the wheel is surrounded by a wooden

vessel, in which the escaping starch milk is collected, and from which it passes into the clearing vessel. The fermented mass is introduced into the washing wheel, which is slowly set in motion by the continual flow of water; the starch is thus washed out, and separated from the residue containing more or less gluten that is left in the wheel. The operation is ended when the escaping water no longer has a milky appearance.

The further purification of the starch is essentially the same as that described for potato starch. After passing through a fine sieve, it is run into the clearing vessel, where the pure starch is deposited at the bottom, the slimy or glutinous starch forms a layer upon it, and the dilute sour water becomes gradually clear. The sour water is then drawn off through taps, and the impure starch which contains particles of gluten, and of the finer membranes of the grain, embryo, etc., is purified by stirring with water, straining and passing over the inclined surface. The purer starch, after removal of the impure layer, is further purified by submitting it several times to stirring with water and settling.

According to Payen, the starch manufacture in Alsace is carried on in a similar way, but without the fermentation, the swelled corn being crushed, and the starch immediately washed out with water. The starch milk so obtained is strained with difficulty, in consequence of the relatively large quantity of unaltered gluten mixed with it; the further purification is effected by settling, and the inclined surface. It is difficult by this method to carry out the purification perfectly, and the yield of starch of the first quality is small, whilst about one third of the whole product is almost worthless.

Yield of Starch.—The following yield of starch is obtained by the respective processes from 100 parts of wheat of equal quality, used either whole or crushed:—

By the Fermentation Process: 42 parts of the finest starch, and 6 to 8 parts of second product; the greater part of the gluten is lost.

By the Alsace Method: 34 parts of fine starch and 18 parts of second product of little value; the greater part of the gluten is lost; the husks, not being altered by fermentation, are of more value as fodder than the fermented, and about 45 parts are obtained in the moist condition.

By Martin's Method: 52 parts of fine starch, 6 parts of second product, and residue, which contains the whole of the gluten, husk, etc., and forms a very nourishing fodder.

Martin's method is therefore distinguished as well by the yield of valuable product as by the complete utilisation of the remaining constituents of the corn. By carrying on the manufacture in connection with agriculture, it is possible to sell only the starch of the harvested corn, and to retain the remaining constituents on the farm.

Manufacture of Starch from Beans.—In preparing starch from this material the beans are soaked during 24 to 30 hours in water, and then crushed between cylinders under a flow of water. The crushed mass is washed in a cylindrical sieve, such as is figured on p. 768, the starch being carried through with the water and the husks remaining. The starch milk is poured upon the inclined surface, where the larger starch granules form a layer, whilst the smaller, together with other matters suspended in the liquor, are deposited in large clearing vessels. This deposit is rich in nitrogenous food material and the whole of the finest starch granules. After the separation of the water it can be made into fodder with the husks retained in the cylindrical sieve; or, with very careful treatment, this substance can be used for human food. Separation of the albuminous matters by means of an alkaline solution is not in this case possible, as bean starch has the property of swelling when in contact with very dilute alkaline solutions; a solution of soda, which would not act upon wheaten starch, converts the bean starch into a paste.

Bean starch is distinguished from wheaten starch by its greater capability of forming a paste, the same effect being obtained with two parts of bean starch as with three of wheaten starch. Linen starched with bean starch remains pliable, and has not the stiffness of that treated with wheaten starch.

Manufacture of Starch from Maize.—The grain of maize is rich in starch and generally richer than wheat. It differs from wheat grain in the individual cells being denser and harder. In order to obtain the starch, therefore, the grain, whole or crushed, must undergo a prolonged swelling in water. The manufacture is then essentially the same as that of bean starch. After washing in the cylindrical sieve the milk is run on to the inclined surface, and the matter suspended in the water is purified by repeated settlings and strainings.

Manufacture of Starch from Rice.—The preparation of starch from rice is carried on principally in English manufactories. The product is much esteemed by laundresses, and preferred to wheaten starch. No other raw material is so rich in starch as rice; but the cells and the starch granules contained in them are so closely cemented

together that their separation cannot be effected by a simple washing and crushing, and an alkaline solution is always used. The rice is allowed to stand in a ½ per cent. solution of caustic soda until it is perfectly softened. The liquor is then drawn off and the softened rice crushed, and afterwards stirred during 24 hours in fresh alkaline solution of similar strength. By this means the other substances are sufficiently swelled to allow of the starch being washed out, which is effected in the cylindrical sieve. The starch milk generally contains granules still cemented together, and in order to remove these the liquor is allowed to stand a short time until the heavier particles have sunk to the bottom, whilst the lighter particles still remain suspended in the water. The milk is then passed on to the inclined surface, and the larger particles are again treated with soda solution.

Uses.—The best kinds of potato starch are used in the sizing of paper, especially those of finer qualities, the preparation of white glucose syrups, the dressing of fine fabrics, the manufacture of white dextrin, and in the preparation of light pastry. The inferior kinds are used for similar purposes, but in cases where the quality is not of so much importance, such as the dressing of cloth, the thickening of mordants and colours in calico printing, the manufacture of vermicelli, as a low priced addition to bread, in the imitation of tapioca, sago, etc. Starch has also formed a very important application in the dusting of moulds in metal foundries. Formerly powdered charcoal exclusively was used for that purpose; but it was very prejudicial to the health of the workmen, the fine splinters of which charcoal consists acting injuriously upon the respiratory organs. The relative softness of starch, the roundness of its granules, and the readiness with which it is acted upon by different liquids in the human body render it free from these hurtful properties. It was introduced into the metal industry by Rouy, the merit of the inventor being recognised by the Academy of Sciences in the award of the Montyon prize.

Potato starch has the disadvantage compared with other starches of possessing a peculiar smell and taste which is due to the presence of a volatile oil. This smell and taste are to many persons not perceptible, but to others they are so objectionable as to render food prepared from such starch unpalatable. According to Martin, this oil can be separated by first treating the starch with a solution of 2 parts of sodium carbonate in 100 parts of water, and then washing it perfectly with water.

BREAD AND FLOUR.

The origin of the art of bread making may be said to be hidden in the mists of antiquity, for although bread is not the form of food that might be supposed to have presented itself most obviously to the human race, it may be inferred that some one or more varieties of it were in use by all the races of men referred to in the earliest records extant. It appears probable that the first approach to bread making was made by steeping grain of some kind in water, pressing it and then drying the mass by natural or artificial heat. Indeed, Pliny asserts that the art of making cakes was not known until long after the process of reducing grain to flour had been discovered. He also alleges that barley was the only grain at first used for food; but Herodotus, on the other hand, says that the Egyptians ate neither barley nor wheat, but a peculiar kind of corn. Although this point cannot now be decided, there is little doubt that all the earlier forms of bread were unleavened, and that the cakes of the patriarch Abraham bore a considerable resemblance to the damper of the modern Australian settler, the corn bread of North America, or even to the oatmeal bannocks and the scones of Scotland. This view is confirmed by illustrations on early Egyptian monuments, where the loaves depicted are of the shape of modern biscuits and have evidently not undergone fermentation.

It would appear, however, that by the time of the exodus, the preparation of unleavened bread in Egypt had become sufficiently common to need special instructions to be given for the preparation of this article of food. Indeed the practice of the art of baking, as a distinct calling, appears to have been carried on by the Jews and two or three neighbouring nations, the Phœnicians, Cappadocians, and Lydians, long before it was introduced into Europe. The Greeks then became also expert in the art, and after the conquest of Macedonia, some of the Greek artizans being carried to Rome, the trade grew into such favour there, that in the time of Augustus, there were upwards of three hundred public bakehouses in that city, almost all of which were in the hands of Greeks. It is stated, however, that even so late as the sixteenth century, unleavened cakes constituted the only bread known in Sweden and Norway.

At the present day, the French and Viennese excel in bread making, and a large number of varieties of fancy bread are made by them besides the coarser kind. In England several kinds of fancy bread, known as bricks, coburgs, cottage loaves and

French rolls, are usually made of the finest flour, and they differ from ordinary bread chiefly in this respect and in the shape of the loaves. In Germany, Russia, and other parts of the continent, bread is commonly made of rye, or a mixture of rye and wheat. Maize is also used in some countries, especially in America and in the East of Europe.

For the preparation of bread according to modern methods, the corn is subjected to a preliminary operation of grinding, and the meal thus obtained is then sifted in order to separate the coarser husky portions from the farinaceous part which constitutes flour.

Under the term flour or meal are generally included all those products that are obtained by grinding and sifting from different kinds of seed, and especially the seed of cereals. By these operations a separation is effected between the different parts of the grain; the greater portion of the interior being converted into flour, whilst the outer layers, the epidermis, etc., together with the adherent portions, are removed by the sieve as bran.

The flour of cereals contains the following constituents in varying proportions:—

Nitrogenous, neutral, organic substances: gluten, albumen, casein, glucin.

Non-nitrogenous organic substances (the so-called carbohydrates): starch, sugar, cellulose, fats, and volatile oils.

Mineral substances: magnesium, potassium, and calcium phosphates; other potassium and sodium salts, and silica.

Bran does not differ in the nature of its constituents from flour, but contains them in different proportions; it being richer in albuminous, fatty, and mineral substances than the internal portion of the grain. In the preparation of flour, therefore, for human consumption, a quantity of most important alimentary material is removed; a more nourishing bread would be obtained if this were allowed to remain in the flour, and if only the most exterior portion—about 4 or 5 per cent. of the whole grain, consisting of the indigestible woody fibres of the pericarp—were removed.

There are a number of different species of wheat; these again have their varieties. For instance, there are—

I. True wheat: the ears growing upon a tough stalk, and the grain separating easily from the grain chaff.

1. Common wheat: *Triticum vulgare.*
   (*a*) Beardless wheat: *Triticum vulgare muticum*, with awnless ears.
   (*b*) Bearded wheat: *Triticum vulgare aristatum*, differing from the preceding in having awned ears.
2. English wheat: *Triticum turgidum.*
3. Horny wheat: *Triticum durum.*
4. Polish wheat: *Triticum polonicum.*

II. Spelt wheat: with a more brittle, easily broken seed-stalk, the grain being shut in close by the chaff, so that it is not easily separated.

1. The typical Spelt: *Triticum spelta.*
2. Starch corn: *Triticum amylum.*
3. One-grained wheat, Lesser Spelt: *Triticum monococcum.*

This is not the place to enumerate the large number of separate varieties, Technically they are divided into three groups according to the properties of the grain, as follows: viz.

(1.) Hard or horny wheat, with hard, dense, somewhat translucent reddish grain, the least hygroscopic giving little bran when ground, and a tolerably white flour, rich in albumen, fat and salts.

(2.) Soft or white wheat, with soft white non-translucent grain, rich in flour, but poorer in gluten, fat and salts than the foregoing, and easily ground to a fine white flour.

(3.) Half-hard white, intermediate in its characters between the two foregoing, without in any decided degree having the properties of either. This group is specially valued for the preparation of flour, because the separation of the bran is easily effected and the groats by grinding yield a very fine white flour.

Structure of the Wheat Grain.—The ripe wheat grain is of a cylindrical form, rounded at both ends, furrowed longitudinally on one side. The exterior of the grain, especially at one end, is clothed with fine hairs. These hairs present most favourable opportunities for the adhesion of spores and fungi which come into contact with them, and thus indirectly lead to the destruction of the grain.

In a cross section of a grain of wheat the unaided eye can distinguish three essential parts; the husk, the mealy portion, and the embryo. The membrane forming the husk or testa envelopes the grain uniformly; it consists of considerably elongated, thickened, and dried cells, as represented in fig. 554. It is too indigestible for human

food, in consequence of the amount of cellulose it contains, but it is rich in nitrogenous substances, fat, and salts. Immediately under the husk is a series of tolerably large closely packed thick-walled cells (*b*), which surround the whole grain and form the gluten layer. These cells are devoid of starch, and are entirely filled with albumi-

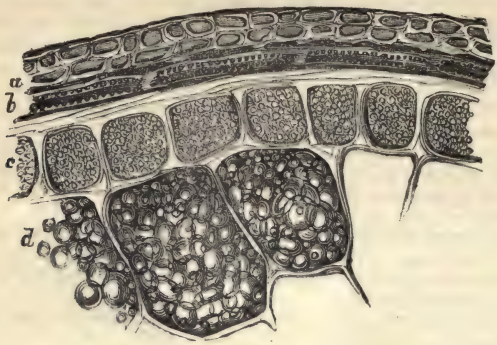


FIG. 554.

nous matters and oil globules; upon treatment with iodine they are coloured yellow. The gluten layer forms the outer circumference of the mealy portion of the grain, the remainder consisting of thin-walled cells filled with starch. Finally at one end of the grain, surrounded by the gluten layer of the mealy portion, is the embryo, from

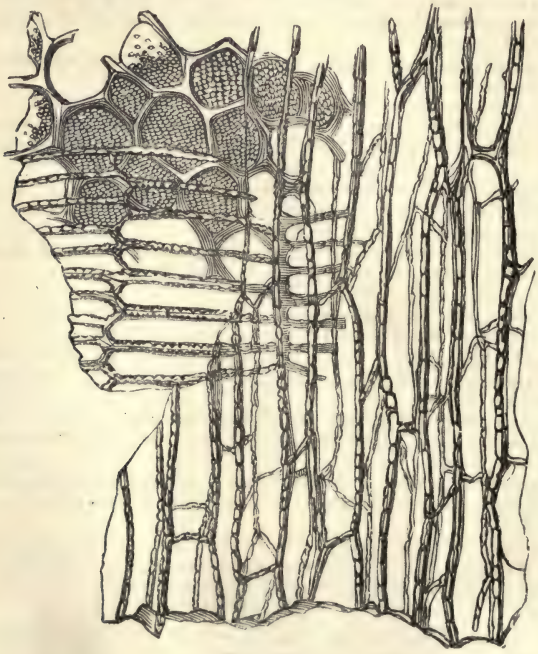


FIG. 555.

which by germination the young plant is developed. Fig. 555 represents a vertical section of the grain of wheat.

Constituents of Corn.—Besides the cellulose which forms the membrane of the separate cells, and which in the seed husk is more or less altered, all kinds of corn contain starch, albuminous substances, fats, sugar, etc., and mineral substances.

The form, composition, and properties of starch are described in another section (see p. 757).

The albuminous matter in wheat is known as gluten; it can be separated from most of the other constituents by kneading under a flow of water. As left by the water, the gluten is greyish white, tough, elastic, very ductile in its unaltered condition and having a faint smell. From damaged grain or flour the gluten is separated with difficulty, being washed away in the flow of water.

Gluten is not a simple substance; as obtained by kneading wheaten flour in water, it always contains the larger proportion of the fat and mineral constituents, the latter being principally phosphates. By treatment with boiling alcohol three different bodies can be separated—vegetable fibrin, casein or mucin, and glutin—all of them belonging to the group of albumenoids. The fibrin is insoluble in boiling alcohol and is therefore left behind when the gluten is boiled. The alcoholic solution being concentrated deposits upon cooling a slimy mass of impure casein. This is removed and again treated with absolute alcohol, which removes all fat, etc., and dries up the insoluble casein to a white earth-like mass. The solution, upon further evaporation, after the separation of the crude casein, yields the gluten, which is soluble in boiling and cold dilute alcohol, but insoluble in ether and absolute alcohol.

In its composition and properties gluten is exceedingly similar to the animal albumenoids, as they occur in flesh, muscle, etc. As a food material therefore it can replace flesh, and for this reason food materials prepared from the varieties of corn have a higher food value in proportion as they are rich in gluten. Notwithstanding its great nutritive value too little importance has been attached to gluten. In order to obtain as white a bread as possible, parts of the grain richest in gluten are allowed to go into the bran. In the starch manufacture the gluten is sometimes intentionally destroyed in order to facilitate the separation of the starch. A more perfect method of separating the starch is described on p. 772, by which the gluten is obtained unaltered. The individual constituents are distributed in very unequal proportions in different kinds of corn, and even in the same kind a great difference may occur, according to the influence of climate, weather, soil, manuring, or harvesting. Thus the hard wheats are always richer in gluten than the soft, and therefore correspondingly poorer in starch. The grain richest in starch, and therefore the poorest in albumenoids, is rice; and the richest in fat are maize and oats. In the following table some analyses of different kinds of grain are brought together, though these only approximate to a representation of the average composition, because considerable variations may be induced by the influence of the conditions of growth. Besides the constituents represented, corn in the air-dried condition always contains from 12 to 15 per cent. of moisture.

Composition of Different Kinds of Grain.

	Starch	Albumen (Gluten)	Dextrin, Sugar and similar bodies	Fat	Cellulose	Ash
Hard Venezuela Wheat	58·12	22·75	9·50	2·01	4·00	3·02
Hard African Wheat	64·57	19·50	7·60	2·12	3·50	2·71
Hard Taganrog Wheat	63·30	20·00	8·00	2·25	3·60	2·85
Half-hard French Wheat	68·65	16·25	7·00	1·95	3·40	2·75
Soft Wheat	75·31	11·65	6·05	1·87	3·00	2·12
Rye	65·65	13·50	12·00	2·15	4·10	2·60
Barley	65·43	13·96	10·00	2·76	4·75	3·10
Oats	60·59	14·39	9·25	5·50	7·06	3·25
Maize	67·55	12·50	4·00	8·80	5·90	1·25
Rice	89·15	7·05	1·00	0·80	1·10	0·90

The flour of cereals is white, bordering upon a yellowish colour; it has an agreeable smell, and is soft to the touch. With half its weight of water it can be kneaded into an elastic homogeneous dough, in which no hard lumps, bran, or sand, should be recognisable by the touch. From this dough the principal constituents of the flour can be separated without difficulty. If a continual stream of water be allowed to flow upon the dough during the kneading the starch is washed out, and can be recovered by allowing the liquid to settle; the gluten finally remains free from starch.

Flour contains from 12 to 18 per cent. of hygroscopic moisture; this is driven off completely by heating the flour to 100°, but moisture is taken up again upon exposure to the air. A high degree of moisture is one of the principal causes of the spoiling of flour, causing it to agglutinate together and become converted into a hard mass;

fermentation also sets in, and through the decomposition of a portion of the gluten the flour then loses its property of making a light, white, palatable bread. Moisture also favours the development of mould, the flour acquiring an unpleasant peculiar smell, and becoming more or less injurious to health.

The finest kind of flour is obtained from several varieties of wheat (*Triticum vulgare*), and it is the kind chiefly used for making bread. The flour of other kinds of grain, such as rye, oats, maize, barley, etc., are also used to some extent for the same purpose. One of the chief characteristics of the flour obtained from these different kinds of cereals is the configuration of the starch granules proper to the several kinds of grain, by means of which it is possible to distinguish one kind of flour from others, and to detect admixtures.

The flour of cereals is subject to many adulterations, such as admixtures of potato flour, pea flour, the flour of maize and buckwheat flour. Bean flour added in considerable quantity imparts to it a greyish-yellow colour, and the bread prepared from such mixed flour has an unpleasant taste and smell. Moreover, the gluten is also acted upon, so that the bread does not rise. An addition of 4 per cent. of bean flour is quite manifest by the heaviness of the bread.

The starch granules of wheat are generally round, disc-shaped, and without any recognisable hilum or distinct annular lines, while others are much smaller, frequently truncated at one end, and present at the rounded end a tolerably distinct hilum with concentric marks, as shown in fig. 556, representing wheat flour as magnified 420 diameters. To the right hand of the drawing is shown the appearance of the cells containing the starch granules.

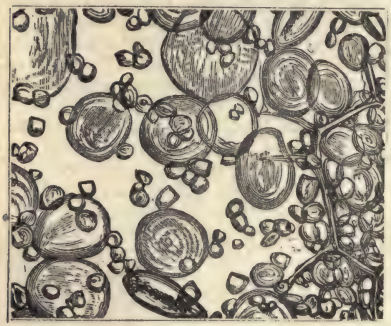


Fig. 556.

The starch granules of the bean (*Faba sp.*), represented by fig. 557 as magnified 420 diameters, are characterised by their uniform or oval shape. The hilum appears very distinctly as a simple or multiple longitudinal fissure, and in bean flour the thickness of the walls of the cells containing the starch granules is considerable, as shown at the lower part of the drawing.

Bean flour is sometimes used to adulterate wheat flour, but palatable bread can be prepared from mixtures containing up to one-third part of bean flour, by adding a larger quantity of salt than is ordinarily used during the preparation of dough.



Fig. 557.



Fig. 558.

The starch granules of the oat (*Avena sativa*) are smaller than those of wheat, and tolerably uniform in size, truncated on several sides, and thus often presenting a polygonal figure (*a a*, fig. 558, which represents oat flour magnified 420 diameters). It is without a recognisable hilum or rings. A characteristic feature of this starch is the aggregation of a number of granules forming rounded masses (*b b*). The tissue (*c*) of the cells is very delicate, presenting a filiform appearance.

The starch granules of barley (*Hordeum distichon*) are partly large and partly much smaller, as shown in fig. 559, representing barley flour magnified 140 diameters.

The larger granules sometimes present distinct rings, and many of them a longitudinal furrow. The tissue of the cells is delicate and filiform.

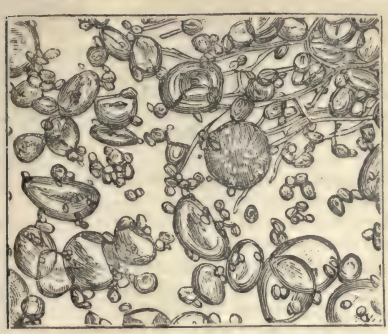


FIG. 559.

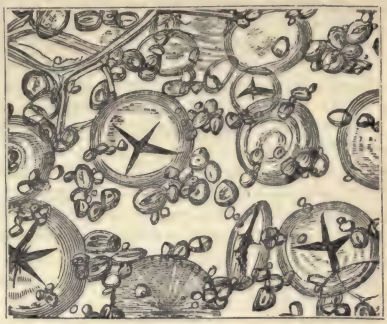


FIG. 560.

The starch granules of rye (*Secale cereale*) are partly large and partly much smaller, the larger granules presenting a very distinctly marked stellate hilum. The tissue of the cells presents some resemblance to that of wheat flour, as shown in fig, 560, representing rye flour as magnified 420 diameters.

The starch granules of Indian corn or maize (*Zea Mays*) are rounded or indistinctly polygonal, often presenting a stellate hilum, as shown in fig. 561, which represents Indian corn flour magnified 420 diameters.



FIG. 561.

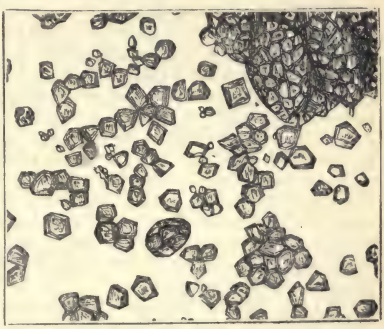


FIG. 562.

The starch granules of rice (*Oryza sativa*) are small and generally angular, with well-marked central depressions, as shown in fig. 562, representing rice flour magnified 420 diameters. The granules are very similar to those of the oat, but are smaller, while the cells in which they are enclosed are angular and separate readily from each other.

Other methods of testing samples of flour and bread have been given by Donny.

(1.) *Adulteration with Potato Starch.*—A thin layer of the suspected flour is moistened with a 2 per cent. solution of potash and examined under a strong magnifying glass or a microscope. The wheat starch undergoes no change, whilst the potato starch swells considerably, retaining the contour of the granule. The change may be rendered more distinct by treating the partially dried mass with solution of iodine.

The presence of potato meal in bread may be detected in a similar manner. If a little of the bread crumb be moistened with potash solution and covered with a glass, the large granules of potato starch, greatly swollen and intensely coloured by the iodine, can, if present, be easily recognised by the aid of a magnifying glass.

(2.) *Adulteration with Rice or Maize Flour.*—The suspected flour is kneaded under a jet of water and the liquid passed through a fine sieve. The starch is collected, washed, and examined, under a microscope. If the sophistication has occurred, the angular granules, which are formed in rice and maize through the excessively filled cells pressing against one another and adhering together, can be easily found. The single granules of maize and rice adhere so closely together that they do not fall asunder, but ordinarily retain the form of the surrounding cells or their fragments.

(3.) *Adulteration of Rye Flour or Bread with Linseed Meal.*—If linseed meal be moistened with a 10 per cent. potash solution, a large number of very characteristic small bodies become manifest, which are of smaller dimensions than potato starch, have a glassy appearance, and are mostly red in colour, and square or oblong in shape. These are fragments of seed husks, and are so characteristic that they can with certainty be found if the rye flour contains only 1 per cent. of linseed meal. In examining the bread or flour for this adulteration a little should be moistened with the potash solution on the object-glass of a microscope. The adulteration of rye flour with oatmeal cake was very prevalent in Belgium and the North of France in the years 1846 and 1847.

(4.) *Adulteration with Buck-wheat Flour.*—This adulteration may be detected with a glass by proceeding in the same way as in testing for maize and rice flour. Buck-wheat flour yields polyhedric masses of starch resembling that of maize; but from this it can be distinguished by the agglomeration of the simple cells.

(5.) *Adulteration of Corn Flour with Leguminous Meal.*—The meal of leguminous plants (beans, peas, vetches, lentils, etc.) always contains the cellular tissue of the seed from which it is prepared, and its characteristic form renders its detection possible. The flour is spread out upon the object-glass and moistened with a 10 per cent. potash solution. The starch of the cereals is dissolved and disappears, whilst the form of the leguminous cellular tissue is made more clear and can be recognised with a glass.

An admixture of the meal of beans and vetches can also be detected through the peculiar reaction when treated successively with nitric acid and ammonia. Bean meal and vetch meal are coloured red, whilst the flours of different kinds of corn acquire a yellow colour. In mixtures containing these kinds of meal red spots are produced in number corresponding with the amount of foreign admixture. The best method of applying this test is to spread out the flour round the sides of a white porcelain vessel; place inside this a smaller vessel containing concentrated nitric acid, cover the whole with a glass plate, and then gently warm them in order to bring the acid vapour in contact with the flour. As soon as part of the flour has become yellow, the small dish containing the acid is replaced by one containing ammonia, the vapour of which is allowed to act for some time. If leguminous meal be present, it soon assumes a red colour perceptible to the naked eye and appearing under the glass in red spots. With pure corn flour only a yellow colour and yellow spots are observed.

For the detection of bean meal and vetch meal in bread an aqueous extract is prepared, which would contain the matters that are coloured red by the action of nitric acid and ammonia. A portion of the crumb mixed with cold water is heated to boiling and thrown on a sieve. After a time the clear liquid is poured off from the sediment, evaporated in a water bath to a thick extract, treated with alcohol, and the alcoholic solution evaporated. There is then left upon the sides of the capsule a layer of the extracted substance, which can be submitted to the successive action of the vapours of nitric acid and ammonia.

(6.) *Detection of Wheaten Flour in Rye Flour.*—There are many places where a tax is levied upon all food introduced, such as flesh, bread, flour, etc. As a rule the kinds of flour principally used by the poorer classes are less highly taxed than others which yield a finer bread suited for the consumption of the more wealthy inhabitants. This renders possible attempts, by representing wheaten flour or mixtures of the two as rye flour, to escape with paying the lower tax. Doubtful cases not unfrequently arise where the taxing officer confiscates a suspected flour, and the expert has to give an opinion on oath whether a sample submitted to him has been prepared from wheat or rye, or whether it only contains an admixture of wheat. The only possibility of a determination depends upon a difference which ordinarily is manifest between the gluten of wheat and the gluten of rye. Whilst the gluten of wheat forms, as a rule, when kneaded, a plastic, elastic mass, the gluten of rye is usually wanting in this property. If a dough be kneaded from rye flour and washed in a stream of water, the dough has a tendency to dissolve and the gluten to be washed away with the starch; whilst that from wheat remains behind as a plastic mass. This is the only difference between normal wheaten flour and normal rye flour. It has already been mentioned that the smallest alteration in the flour, through sprouting of the grain or fermentation of the finished product, is at once shown in the changed properties of the gluten, which loses its toughness and elasticity. The wheat gluten then behaves exactly as rye gluten, and is washed away by a stream of water.

The tenacious character of wheat gluten can, however, be restored by various agents. If flour from sprouted wheat, or fermented flour, be kneaded with common salt, lime water, or alum, the gluten recovers its original toughness and elasticity. Rye flour behaves in a similar manner. If a dough be made of rye flour with the addition of a small quantity of lime water, and washed. the gluten obtained has all the properties of wheat gluten, or at most is a little less elastic.

As therefore the two kinds of gluten differ so little that wheat gluten can be changed by moisture or fermentation so as no longer to be distinguishable from that of rye, whilst rye gluten may be altered by a small quantity of lime acquired from the soil in which the plant grows, the small differences between them cannot be sufficiently characteristic to furnish scientific evidence for a court of justice. The light spongy property of well-made bread is dependent upon certain qualities of the gluten. When obtained from good flour this is elastic, soft, pliable, and ductile; upon rapidly heating it to 200° it swells up considerably. These properties are met with principally in wheaten flour; from other kinds of meal an adherent gluten cannot, as a rule, be separated. Every change in flour induces a change in the properties of the gluten present in it, so that from fermented flour light bread cannot be prepared. These changes may commence as early as the harvest, through continued wet, sprouting, etc.

The properties of the gluten in various kinds of flour may also be turned to account in comparing the value of different kinds of flour and detecting adulteration.

Potato Flour.—For a long time it was sought to bring the potato by desiccation into such a form that it would be preserved from spoiling, and to prepare from it a concentrated food that could be transported for long distances—such as sea voyages—without the necessity of carrying 75 per cent. of water with the 25 per cent. of food material. No great success was attained in this direction until Chollet invented a method by which a faultless material could be prepared at a comparatively low cost.

Potato meal is not very liable to spoil, and will keep for a considerable time in dry places. A considerable quantity of this article is imported from France into England, and is used specially in the provisioning of emigrant ships.

Bolland's Test for Wheaten Flour.—25 grams of flour are kneaded into a dough with 12 or 13 grams of water; the mass is then allowed to stand some time in order to allow the gluten to swell completely, which in warm weather requires about half an hour and in winter 1 hour. The dough is then kneaded under a gentle stream of water until the water flows off colourless, and the moist gluten is well drained. From this 5 grams are weighed off, rolled into a ball, and allowed to drop on to the bottom of a small brass cylinder, the interior of which is slightly smeared with oil. The cylinder is then placed in an oil bath, previously heated to 210°, in order to heat the gluten rapidly. The vaporisation of the enclosed water causes the elastic mass of gluten to puff up and lift a light piston to a distance corresponding with the increase in volume. This increase is proportional to the quality of the flour, and amounts to from 2 to 6 times the original volume of the gluten. The experiment can be controlled by taking out the gluten remaining in the cylinder, drying it completely at 100°, and taking its weight.

If it is desired to estimate the quantity of starch also, the wash water from the gluten is poured upon a fine sieve in order to retain any detached gluten and traces of bran, and the starch is allowed to settle. After clearing, the water is decanted off, the starch is washed once with pure water, dried, and weighed.

With the estimation of the starch a test for adulteration with potato-starch flour can be easily combined. For this purpose the starch is washed with a small quantity of water into a conical glass, and allowed to settle. The larger and heavier granules of potato starch sink to the bottom most rapidly, and are found at the extreme point of the cone formed by the settling of the starch. The upper portion is removed with a spatula, and the lower layers are submitted to a microscopical examination, when the potato starch can be at once recognised by its form and size.

Preservation of Corn.—In countries where agriculture constitutes the chief occupation of the people, and where a relatively small number of inhabitants cultivate a large area of land, considerably more corn is produced than is consumed, except in years when the crop fails. In more thickly populated countries also there are sometimes years of plenty when the produce exceeds the demand. Under such conditions the storing of corn and its protection from decay become of great importance.

Care for the preservation of corn needs to commence as early as the harvest; for frequently the basis of after decomposition is laid at that time, and a large proportion of grain becomes injured through negligent treatment. By exposure to moisture the corn begins to sprout in the ear, and its value is diminished; or it is attacked by fungi and becomes mouldy and rotten. One method of preventing rain from damaging corn consists in standing a number of sheaves upright together, and inverting above them another sheaf, in such a manner that the downward hanging ears form to some degree a roof for the others. Sometimes four or more sheaves are placed upright close together, or one is placed in the middle, and the others are packed around, and se-

cured closely together at the top by a band (fig. 563), and then covered with another sheaf (fig. 564). The grain is thus perfectly protected from wet, as the rain flows off



Fig. 563. Fig. 564.

rapidly from the downward hanging straw of the covering without penetrating. The sheaf further presents the great advantage of favouring the full maturity of the corn, the sap constituents contained in the stalk becoming concentrated in the grain, and a better product yielded. On the other hand, more labour and time are required by this method than by the ordinary ones, and the scarcity of labour at harvest time prevents it being generally adopted, notwithstanding its acknowledged advantages.

Equal protection is afforded by the stacking of corn, if the stacks are protected in a similar manner. Here the sheaves are not arranged in a circle, but in two rows leaning against each other, with the ear upwards; above these is placed a covering of sheaves with the ear downwards. The rain is thus kept off, whilst free ventilation is secured. By this method also the corn can be harvested before it is perfectly ripe, and the quantity and quality of the grain augmented.

Not only during the harvest, but in the granary also, corn is exposed to many causes of decay, which require to be combated by the greatest care and by different methods of preservation. Notwithstanding the ordinary precautions, frequently upwards of 12 per cent. of the harvested corn is lost in a single year.

The greatest injury to corn is caused by insects; moisture also induces fermentation and putrefaction; and further damage is done by rats, mice, and similar animals.

The principal destroyers of corn are the black corn worm or corn weevil (*Curculio granarius*, L.; *Calandra granaria*, Fab.; *Sitophilus granarius*, Schœn.), and the white corn worm, or corn moth, or wolf (*Tinea granella*, L.; *Alucita granella*, Fab.)

The black corn worm, or corn weevil, belongs to the tribe *Rhyncophus*. It is about a twelfth of an inch long; when young it is light brown, but it gradually becomes darker, and at last almost black. During the winter the weevil remains in chinks and crevices of the rafters and boards; but at the beginning of the warm weather it comes forth and the female lays 100 to 150 eggs, each one in a separate grain just under the husk. From these eggs shortly afterwards escape worms provided with strong mandibles, which using the contents of the grain for food and the hull for a domicile, pass there their pupa existence. Six weeks after the laying of the eggs the perfect insects are formed, and other similar augmentations take place. It has been calculated that a dozen pair of these pests will bring forth during the warm weather 75,000 individuals. Should this dozen pair nestle in five or six bushels of wheat and each of their progeny destroy only three grains, the loss would amount to at least 12 per cent. The destruction caused, however, appears somewhat to depend upon the insect being left undisturbed, and to be diminished by frequent shovelling and sifting of the corn. The insect, moreover, can with difficulty withstand strong currents of air, especially in the winter; a thorough ventilation of the granary therefore is one of the most certain preventives against its ravages.

The white corn worm, or corn moth, is a small moth with front wings of a light yellow colour spotted with black, and dark grey hinder wings. It makes its appearance with the beginning of warm weather; during two weeks the female lays eggs, depositing them either singly or two together in a grain of corn, showing a preference for rye. After a short time from each egg is hatched a yellow worm, which

devours the grain, then passes to another, and so on until the end of the summer. It passes the winter as a caterpillar, enters the pupa state in the spring, and is transformed at the commencement of summer into the perfect moth. Turning and sifting of the corn is only an imperfect remedy against these troublesome insects, as only a portion of them are destroyed by the operation.

Besides injury by insects, the grain is affected by fermentation and decay. If it is too fresh when threshed and brought damp into the granary, it easily becomes heated; mould accumulates, setting up different kinds of fermentation, which generally end in putrefaction. Different methods have been suggested for the preservation of corn, and carried out with more or less satisfactory results. They aim at:—

(1) Thorough airing or ventilation of the corn by continued motion.

(2) Perfect drying by means of heated air.

(3) The preservation of the grain in grain pits dug in dry soil. This method is adopted in southern countries—Southern France and Spain and Africa—with satisfactory results, but it is only suited for localities possessing a sufficient dryness of soil.

For these different methods the following forms of apparatus have been constructed:—

Vallery's Apparatus (*grenier mobile*) consists of a large wooden cylinder (*d d d d*, fig. 565, transverse section; fig. 566, longitudinal section), the frame being made of strong staves bound together with iron hoops. Within this is a much smaller cylinder (M M), bound to it by strong cast-iron end plates, which at the same time close the ends. Round the circumference of both cylinders are a large number of oblong openings (*o o*), covered with wire gauze. The space between the two cylinders is partitioned off into eight equal divisions (A, B, C, etc.) for the reception of the corn, and each of these is again divided by three cross partitions into four small compartments, making thirty-two in all. The cylinder rests upon a strong wooden frame (*g*), and can be easily rotated upon its axis by means of a cogwheel (*b*), working a toothed wheel (*a*) at one end. At the same time as the cylinder is slowly revolving the shafts of the ventilator (*f*) are set in motion very rapidly by the driving straps (*i e*). The ventilator being in communication with the interior of the smaller cylinder (M), air is thus drawn through the openings (*o o*) in the outer cylinder, through the corn, and finally through the inner cylinder to the ventilator. The strong current of air dries the corn perfectly; whilst the motion destroys the worms and rubs off the adhering eggs which fall through the meshes. For filling and emptying the apparatus some of the wire-gauze coverings in each compartment are fixed in sliding frames. The cylinder is about 30 feet long and 15 feet in diameter.

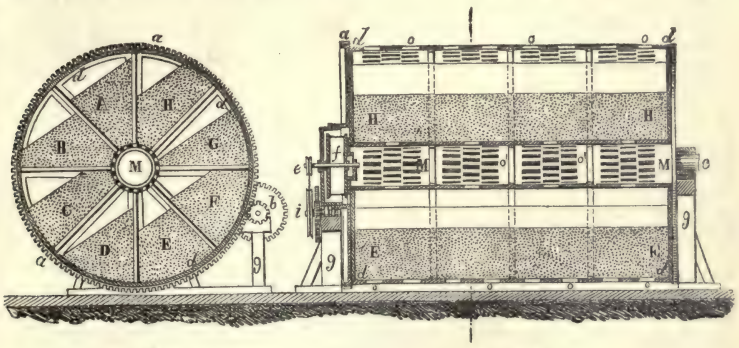


Fig. 565.

Fig. 566.

The inner space will hold about 3,850 bushels, but in order to allow of the movement of the grain only about 2,750 bushels are used.

Coninck's Apparatus is based upon the same principle of agitation and ventilation, but is differently constructed. It is a square brickwork shaft, having walls each about 10 feet wide and 50 feet high, and holding nearly 3,400 bushels. The shaft is divided by seven horizontal layers of beams which act as supports for strong plates of zinc. Two of these, contracting funnel-wise and not far apart, are placed in each interval between the joists, so that the floor thus formed is broken by long slits, the slits being wider in the lower than in the upper floors. When all the compartments are full of corn, if a small portion, about ten per cent. of the whole, be

allowed to run out rapidly at the bottom, the entire mass is set in motion. But through the unequal width of the interstices this movement is not uniform, the corn passing out from each compartment more rapidly than it is replaced from the one above, and this causes a current of air to be drawn in through side openings covered with wire-gauze. The corn which runs out from the lowest compartment is raised to the top by a chain-pump arrangement.

Huart's Apparatus.—An apparatus has been introduced into the military department in Paris very similar to the preceding, but having sheet-iron sides instead of walls. Each shaft is divided by 24 to 28 lattice-work screens made of iron rods. The corn is set in motion by the opening of a door in the lowest compartment.

Devaux's Apparatus is also an iron shaft 32 feet high and 4 feet in diameter, but it differs from the preceding in having its sides perforated with small holes. A pipe $\frac{1}{2}$ to $\frac{3}{4}$ inch in diameter, closed at the top and finely perforated over its whole surface, passes through the shaft, and ventilation is effected by forcing through it a strong current of air.

Preservation in Pits (*Silos*).—Earth pits or silos are only suitable for keeping corn in hot countries. Brickwork silos, that can be closed air tight, or large metal receptacles, have also been recommended. In order to protect corn placed in them from decay several methods have been described. Persoz and Petitot recommend the introduction of quick lime in baskets covered with wire gauze; the lime absorbs moisture, so that even sprouted corn can be thus preserved. An experiment made by Petitot with wheat harvested in wet weather showed that at the end of five years it was perfectly sound and fit for making into bread.

According to Doyère and Garreau the most certain means of extirpating the corn worm in such silos is by using a small quantity of bisulphide of carbon. About 1 part by weight to 50,000 of the corn is sufficient to destroy all insects, and even the eggs in five or six days. About 5 parts to 100,000 will have the same effect in twenty-four hours.

Production and Preservation of Potatoes.—The potato is unquestionably one of the most useful crops in agricultural economy, inasmuch as it leaves the ground upon which it is cultivated in capital order for the next crop in rotation, and in regard to yield is excelled by no other crop. A comparison of the yield of different crops shows that the potato takes the first place, as may be seen from the following table:

	Average Production per Acre in Tons	Total Dry Matter in Cwts.
Potatoes	21 to 28	$5\frac{1}{4}$ to $6\frac{1}{2}$
Jerusalem artichoke	19 „ $23\frac{3}{4}$	$3\frac{3}{4}$ „ $4\frac{3}{4}$
Turnips	30 „ 40	$4\frac{1}{2}$ „ 5
Swedish turnips	18 „ $22\frac{1}{2}$	$1\frac{1}{8}$ „ $1\frac{2}{3}$
Wheat	$1\frac{1}{4}$ „ $1\frac{1}{2}$	1 „ $1\frac{1}{3}$

The potato crop and the quality of the potatoes depend upon the soil and the state of the weather, the amount of starch yielded by potatoes varying so considerably that it is hardly possible to make an estimate of the yield of any sort of potato. According to some experiments of Payen, the yield of starch from various kinds of potatoes grown in France varied from $3\frac{1}{2}$ to 5 tons per acre. The Rohan potato is still more productive in starch, but its tubers are very watery, and on this account it is not much liked by the manufacturer. Scotch shaws, a very favourite early potato, is for the most part used as food; it is, however, much prized by starch manufacturers, as its early maturity enables them to begin work early in the year.

The starch contents of gathered potatoes does not remain constant, but decreases continually, owing to the growth of the tubers. Potatoes laid in heaps generate heat, and begin to germinate, producing rootlets and young shoots. All these processes depend upon the formation of new cells, the material for which is supplied by the starch in the potato, it being converted into the cellulose constituting the membrane of the cells. Hence it happens that potatoes which immediately after harvesting yield 17 to 18 per cent. of starch, yield in January and February only 15 per cent., and in March and April not more than 13 per cent. The starch manufacturer, therefore, endeavours by suitable storing to suppress germination in the potatoes as completely as possible, and also so to conduct his operations as to finish the starch manufacture within four months of the harvest.

In order to protect the potatoes as far as is possible from spontaneous changes they are stored in dry chambers, the temperature of which is low without sinking to zero, and which are protected as completely as possible against changes of tempera-

ture. Cellars and pits in the earth are used for this purpose. It is necessary in storing the potatoes to keep out diseased and rotten tubers, as these would affect the sound ones. The construction of the earth pits depends upon the soil; where this is moist the pits are made shallow, ditches are dug round them, and the potatoes are piled up partly above the mouth of the pit, and covered with the earth taken from the ditches. Where the soil is dry the pits are made deeper. The pits are generally about 5 feet wide at the bottom, and at the mouth 6½ feet. The walls or sides of the pits being sloped. The depth of the pits is about 3 feet; the length varies between 60 and 320 feet.

In some manufactories, potatoes are stored in brickwork pits, and covered either with earth or straw. Dailly employs pits of this kind, sunk 5 to 6½ feet deep in the earth, 160 to 200 feet long, 25 feet wide, and 8 to 10 feet high, a slate or thatched roof protecting them from rain and moisture. The pits are filled and emptied through openings in the walls, which are closed in winter with straw to keep out the cold. Although the first cost of such pits is considerable, the expense of the yearly construction of the simple pits is saved.

Brickwork pits are especially serviceable where the soil is moist. They are, however, little used in Germany, the agricultural system in that country seldom allowing sufficient time during the harvest for conveying the potatoes to the manufactory from distant parts of the farm; the potatoes are simply buried in the earth, and in winter when the weather permits are transported to the manufactory in quantities sufficient for a few days.

In burying potatoes special care must be taken that they are sufficiently protected from frost, which may be secured by sufficient warm covering, and careful reclosing of such pits as have been opened but not emptied. Should any potatoes be frozen, however, for the manufacture of starch it is better to use them in the frozen state than to thaw them, as this renders the cells soft, and the membranes, which were before impenetrable by the sap, allow the sap to escape freely through them. Such potatoes are but incompletely torn in the rasping machine, and since starch only escapes from open cells a loss of material is occasioned. When frozen potatoes are worked up, the teeth of the rasping machine may, perhaps, suffer a little, but the proper quantity of starch is extracted.

Composition of Potatoes.—It has been already mentioned that the starch contents of potatoes is influenced by a number of circumstances; the same may be said of the other constituents of the potato. For this reason approximate figures only can be given for their percentage composition. The following is the average percentage composition of good potatoes:

Water	74·00
Starch	20·00
Epidermis, cellulose, pectose, and colouring substances	1·65
Albumen and other nitrogenous substances	2·12
Fat	0·11
Sugar, resin, volatile oil	1·06
Salts and ash constituents	1·06
	100·00

The amount of starch in different sorts of potatoes grown under equal conditions varies between 12 and 14 per cent.; although the fluctuation is not so great in potatoes of the same kind it is liable to considerable variations. For this reason, therefore, it is important that the starch manufacturer should examine the potatoes to be used, so as to ascertain their quality.

The testing of the starch contents of potatoes is based upon the fact that starch has a considerably higher specific gravity than water; the richer, therefore, the potatoes are in starch, the greater is their specific gravity. A table has been constructed, showing the percentage of starch in potatoes of different specific gravities. The determination of the specific gravity is accurately accomplished with a very simple apparatus. It consists of a glass cylinder, having a capacity of about 5 pints, the upper rim of which is ground; the cylinder itself is supported upon a wooden foot. The foot is furnished with three screws for bringing the cylinder into an exactly upright position. The volume of the cylinder up to a certain point is determined once for all by measuring with water. This point corresponds with the length of a finely pointed brass rod, which is fastened vertically upon a small brass plate. The cylinder is brought into a perfectly upright position by means of the screws at the foot, so that the bubble in a water-level laid on its edge shall rest exactly in the middle. From a measure graduated to cubic centimetres so much water is then poured in as to nearly but not quite reach the point corresponding with the length of the brass rod, which should be previously scratched on the side of the cylinder. The brass rod is

then suspended in the cylinder, and water is carefully added drop by drop until the point of the rod exactly touches its image reflected on the surface of the water. As the brass rod marks an invariable length, the expansion through changes of temperature being too inconsiderable to be taken into consideration, a point can thus be fixed, the volume of the cylinder up to which could be determined by measurement once for all.

In making the test, about five pounds of potatoes are selected which fairly represent the average of the bulk. These are washed perfectly clean, a brush being used if necessary, then dried with a clean cloth, and the weight taken in grams. They are then placed in the empty cylinder, previously brought perfectly upright, and water added until the surface comes exactly into contact with the point of the rod. The quantity of water used will be less in proportion to the larger volume of the potatoes. In a case where the volume of the cylinder up to a fixed point was 3,185 cubic centimetres, and the sample of potatoes used weighed 2,960 grams, if 514 cubic centimetres of water were used the volume of the potatoes used would be $3,185 - 514 = 2,671$. The specific gravity of the potatoes could then be easily calculated: $\frac{2960}{2671} = 1{\cdot}108$. According to the following table, which is based on numerous experiments, a specific gravity of 1·108 would correspond with 20·61 per cent. of starch contents:

Table of the Average Contents of Potatoes in Starch according to their Specific Gravity.

Specific Gravity	Contents in Starch per cent.	Specific Gravity	Contents in Starch per cent.	Specific Gravity	Contents in Starch per cent.
1·072	12·22	1·089	16·11	1·106	20·13
1·073	12·45	1·090	16·35	1·107	20·37
1·074	12·67	1·091	16·58	1·108	20·61
1·075	12·90	1·092	16·81	1·109	20·85
1·076	13·12	1·093	17·05	1·110	21·09
1·077	13·35	1·094	17·28	1·111	21·33
1·078	13·58	1·095	17·52	1·112	21·57
1·079	13·81	1·096	17·75	1·113	21·81
1·080	14·04	1·097	17·99	1·114	22·05
1·081	14·27	1·098	18·23	1·115	22·30
1·082	14·50	1·099	18·46	1·116	22·54
1·083	14·73	1·100	18·70	1·117	22·78
1·084	14·96	1·101	18·93	1·118	23·03
1·085	15·19	1·102	19·17	1·119	23·27
1·086	15·42	1·103	19·41	1·120	23·52
1·087	15·65	1·104	19·65	1·121	23·76
1·088	15·88	1·105	19·89	1·122	24·01

Potato Disease.—The special malady of the potato, known as the potato disease, first broke out in the United States in 1843; two years later it made its appearance in Europe, and rapidly spread over the various countries. The disease is due to the penetration and growth of a fungoid parasite, *Perenospora infestans* (the *Botrytis infestans* of Montagne). The mycelia of this fungus penetrate either through the fissures in the plant or directly through the membrane of the outer cells, and spread with extraordinary rapidity in the tissue, where they fructify and throw off myriads of new spores. From the leaves the fungus spreads over the stalk to the tuber, where it impoverishes the cells by dissolving the starch, and absorbing the remaining mineral and organic substances. In this condition the fungus may lie dormant in the tuber during the winter, and in the spring sets up a fresh growth. But ordinarily the destruction commenced by the fungus is accompanied by a putrefaction which destroys the entire tuber and very frequently the fungus with it.

If a potato only just attacked be cut, brown spots can be seen which spread from the stalk, where they are most developed, to the extremity. These discolorations are due to the parasitic vegetation which fills the tissues, making it more resistant and less transparent. If such a potato be boiled for four hours in water, the parts that have not been attacked by the fungus appear mealy and soft, as is usual with a sound potato; but the spotted parts, the colour of which is intensified by the boiling, become firmer, and can no longer be crumbled between the fingers.

By the action of the fungus the starch is dissolved and converted into carbonic acid and water, whilst the albumen, fat, etc. are used in the formation of tissue. The disappearance of the starch can be recognised by the naked eye in a very thin section,

but it can be made more evident by boiling such a section in water, and treating it with an aqueous solution of iodine. The parts yet unattacked are coloured intensely blue, whilst the parts in which the fungus occurs is not coloured. If the brown portion of the boiled tuber be removed and treated for several hours with boiling water acidified with sulphuric acid, the residue remaining after drying has the same composition as has been observed in other fungi, containing 8·75 per cent. of nitrogen.

The disease can easily be communicated by contact with a diseased potato, especially to freshly cut surfaces. During the preservation it readily spreads in the pits; the greatest care is therefore taken not to bury potatoes visibly diseased with the sound ones. Should the disease break out in the pit, the only method to limit the injury is to work the potatoes up as rapidly as possible, as the loss increases from day to day. Many of the starch granules become hollowed out by the fungus, and set up a fermentation in the liquid. This fermentation can be controlled by adding 0·1 per cent. of sulphurous acid to the liquid, which stops the agitation in the liquor, and facilitates the settling of the starch. Such potatoes can be used in the preparation of spirit.

The pulp remaining from the working up of diseased potatoes may be used without danger as fodder, and it can be preserved in pits without decomposing.

The Preparation of Bread is in general extremely simple; but it involves certain difficulties if the object be to obtain a spongy, light, well-flavoured bread. The ancient art of bread-making, which in many localities is still practised exactly in the same manner as it was a thousand years ago, has undergone successive improvements, and already in some places has taken rank as a large industry, being carried on with improved machinery. It is not possible to give here an exact description of bread-making, since many modifications depend upon the habits of the consumer, the raw materials, and the products to be obtained. Only the essential points in the manufacture will therefore be noticed, and especially some of the numerous improvements in the machinery used.

The separate stages of the operation by which flour is converted into bread are—the making of the dough, kneading, fermentation, and baking.

The making of the dough consists in a uniform saturation of the flour with water. The soluble portions of the flour, *i.e.* the sugar and dextrin—the proportion of which is increased by the action of a peculiar principle (diastase) on a portion of the starch—the albumen, and the casein, are dissolved, and the gluten, by the absorption of water, commences to swell. Dough kneaded with water only would yield a close, heavy, dry bread. But, by the addition of yeast, fermentation is induced, which converts the sugar into alcohol and carbonic dioxide. The gas evolved increases the volume of the dough and induces the rising; for since the escape of the gas is hindered by the toughness of the gluten, it forms small bubbles wherever it is evolved throughout the dough, and so produces the sponginess of the finished bread.

The fermentation of the dough is set up by an alcoholic ferment, beer yeast or pressed yeast. Beer yeast is, however, only used exceptionally on the Continent, because, by the addition of hops, it acquires a bitterness which it communicates to the bread. A more suitable yeast is prepared artificially from an infusion of malt in which fermentation is set up by the addition of pure yeast. The preparation of such artificial yeast is subsequently described under 'Spirit Manufacture.' In the preparation of bread yeast is not always added; but a portion of the dough in which fermentation has commenced is reserved for the following operation. This sour dough is then added to the fresh dough, and being rich in ferment induces fermentation in the whole mass.

If sour dough, however, be allowed to stand too long, not only alcoholic but lactic acid fermentation is set up, and it would then induce the same process in the bulk of the dough to which it might be added. In order to confine this secondary fermentation within the requisite limit, care must be taken that in the sour dough the conditions most favourable to the alcoholic fermentation are always present. This is effected by continually adding, at short intervals, fresh material in the shape of flour to the dough, an operation which is known as reviving the sour dough.

The sour dough from previous bakings is kept in a moderately warm place, at as uniform a temperature as possible. It is allowed to stand for seven or eight hours, during which time it gradually increases in size, and gives off a faint alcoholic odour. The first reviving is then effected by kneading with it sufficient flour and water to bring the dough to double its former volume; but no more water is used than necessary, in order to leave as stiff a dough as possible. After about six hours the volume of the dough is again doubled by a second reviving, and a somewhat larger quantity of water is added to soften the dough. Finally it undergoes a third reviving. The additions of flour are so regulated that in winter the sour dough contains one half and in summer one third of the entire quantity of flour to be used.

When bread is made in this way the sour dough is stirred up with the whole amount of water to be used in the baking, and kneaded until no more lumps are perceptible in the mass. Flour is then added in small portions, and continually and vigorously kneaded, until the whole of the flour is uniformly distributed throughout the sour dough. The dough gradually becomes more stiff and dry, and it requires considerable power and skill to make the mixture uniform. Nowhere in the mass must any dry spots remain, since they would be found as lumps of flour in the finished bread; whilst, above all, the sour dough must be thoroughly distributed, as it is only by actual contact with the remaining dough that fermentation takes place. Another object is attained during kneading in the introduction of as much air as possible into the dough; this air upon being heated expands and contributes to the sponginess of the bread. During the kneading salt is added. This is either strewed in the dry state, or more suitably, in order to secure a better distribution, dissolved in the water used in the first working of the sour dough. The quantity of salt used varies according to the taste of the consumer. The Parisian bakers use about 1 part of salt to 300 parts of flour.

By the addition of salt, the quality of bread made from flour of which the gluten has lost some of its plasticity, is considerably improved. Bread prepared from sprouted corn with but little salt added is close and heavy. But by using 3 parts of salt to every 100 parts of such flour, the gluten recovers its original elasticity and the bread is spongy and light. A sound, nourishing and well-flavoured bread can be prepared from a mixture containing rye flour and bean meal, if 2½ or 3 parts per 100 of salt be added.

The dough being prepared, it is divided into portions corresponding with the size of the loaf. On an average 115 or 116 parts of dough yield 100 parts of bread; large loaves, however, require somewhat less, as they lose proportionally little moisture in baking, and small loaves more. The separate loaves are then lightly powdered with flour, and placed in the neighbourhood of the oven, the warmth of which favours the fermentation. The fermentation is not continued longer than is required for the rising of the bread, but is arrested as soon as the requisite point is reached by placing the dough in the oven. If the dough were allowed to stand longer, the carbonic acid formed would gradually escape, and the dough would sink together; further, the alcoholic fermentation would be followed by the acetic fermentation, and a badly flavoured bread would result.

During the baking various changes take place in the dough. The enclosed gases, carbonic acid and air, are increased in volume very considerably by becoming heated, and as the tough dough mass does not allow them to escape, it is puffed up and increased in size; so that the sponginess of the bread induced by the fermentation is still further increased by the baking. The alcohol formed during the fermentation behaves in a similar manner, being converted into vapour at the temperature of the oven. The starch swells in contact with water and combines with it at a high temperature, and the previously soft moist dough becomes firm and dry. By the strong radiated heat a portion of the starch is converted into dextrin; this dissolves in the moisture, and upon the evaporation of the latter it remains as a close shining crust upon the top layer of the bread. Lastly, a portion of the dextrin or of the starch is changed into yellow or brown substances, which impart to the crust its characteristic colour.

According to Mège Mouriès, the internal part of the perisperm of the grain, and consequently the bran, contains a peculiar nitrogenous principle capable of acting as a ferment, which he has named cerealine. Like diastase, cerealine has the property of liquefying starch, which is converted into glucose and dextrin, the glucose in its turn being transformed into lactic, acetic, butyric, and formic acids, which partly dissolve the gluten. To this action Mège Mouriès attributes the inferior cohesion of the crumb of bread made from meal containing bran, and its colour. In order therefore to utilise the whole of the farinaceous substance of wheat in the preparation of white bread, he proposes to remove the cerealine before sufficient time has elapsed for it to have been converted, by exposure to the air or otherwise, into a ferment. At first he effected this by submitting about 20 per cent. of the groats, after the removal of about 70 per cent. of fine flour, to vinous fermentation, by which the cerealine was destroyed. More recently he has adopted the plan of diluting the last 8 or 10 per cent. of groats with five or six times its weight in water, and precipitating the cerealine with a solution of common salt.

Although the rising of the dough and the resulting sponginess of the bread is, as a rule, produced in the above manner, various plans have been suggested for attaining the same end without submitting the dough to the process of fermentation. The incorporation with the dough of a solution of bicarbonate of ammonia, which is subsequently completely converted into vapour by the heat of

the oven, yields a bread that is very porous, in consequence of the expansion of the gas, but which is not spongy. Moreover there is generally a trace of the ammonia retained in the bread. The production of an evolution of carbonic anhydride by the admixture with the dough materials of a certain quantity of hydrochloric or tartaric acid and bicarbonate of soda has also been recommended. But bread made in this way without fermentation is heavy and clammy, and differs in many respects from fermented bread. The use of tartaric acid, with the resulting formation of tartrate of soda in the bread, is open to obvious objections.

One method of preparing an unfermented bread, invented by Dauglish, has however met with a certain amount of acceptation in this country. It consists in kneading the flour and salt in water charged with carbonic anhydride under a pressure of ten or twelve atmospheres in a closed vessel kept at the same pressure. When this kneading has been carried far enough to impart to the dough the requisite tenacity, the pressure is removed; the gas at once seeks to recover its normal volume, and in doing so raises the dough. In consequence of the low temperature at which dough thus prepared is placed in the oven, and the fact that after the first sudden expansion it undergoes a slow springing during heating, until it reaches the boiling point, it has been found necessary to construct a special oven for its baking. This oven is heated through the bottom, and is furnished with the means of regulating the heat at the top. The bread is cooked through the bottom, and when this is nearly completed the top heat is applied and the crust formed.

Baking ovens are constructed in the most diverse manner and for different kinds of fuel. The simplest form, which has obtained from the most ancient times, and is still very much used, consists of an elliptical hearth, either horizontal or sloping in front, and spanned by a flat arch, the front opening being used both as a fire door and smoke draught. The oven is heated by kindling a fire of wood or coals upon the hearth, fresh additions of fuel being made until the required temperature is attained. The fuel is then withdrawn, and the oven being purified from the ashes, it is ready for the reception of the bread.

The oven ordinarily used by bakers in London is shown in figs. 567 (longitudinal

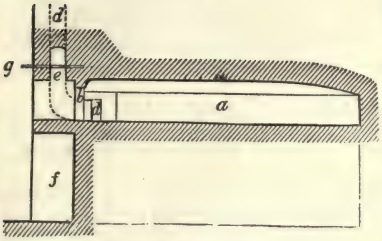


Fig. 567.

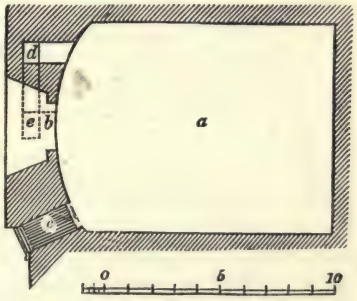


Fig. 568.

section), 568 (plan), and 569 (front view). *a*, is the body of the oven; *b*, the door, *c*, the fire grate and furnace; *d*, the smoke flue; *e*, the flue above the door to carry off the steam and hot air when withdrawing the bread; *f*, recess below the door, for receiving the dust; *g*, damper plate, to shut off the steam flue; *h*, damper plate to shut off the smoke flue; *i*, small iron pan over the fireplace for heating water; *k*, ashpit. The flame and hot air from the fire (*c*) sweep along the right-hand side of the oven to the back, by which they are reflected to the left-hand side and thence escape into the flue (*d*). When the oven is sufficiently heated, the fire is withdrawn, the flues closed by the damper plate, and the dough introduced.

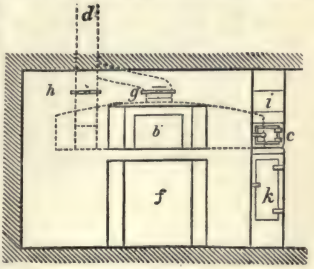
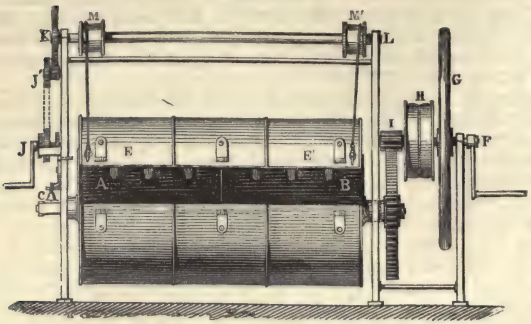


Fig. 569.

In recent times many improvements have been made; the dough is kneaded by machinery instead of by hand labour, and the old oven has been altered in many ways. All these improvements, however, have hitherto been but little used. Some of the more important alterations in the apparatus for kneading and baking are the following:—

Moret's kneading machine is represented in figs. 570 and 571. It consists of a strong iron cylinder (A B, fig. 570), divided into portions by a partition. Inside the cylinder is an iron shaft (*a*, fig. 571), provided with iron arms, (*a*, *b*). The sides of the cylinder are also furnished with similar arms (*d d'*), which are so arranged that when the cylinder is set in motion they pass between the arms of the shaft. The cylinder can be closed by a hinged cover. Sour dough, flour and water are placed in both the compartments (A B), and the cylinder is caused to make four revolutions per minute during eighteen minutes, by the end of which time the kneading is completed. An automatic mechanism registers the number of revolutions, and upon the completion of each thirty-six revolutions gives a signal on the bell (*c*). The cylinder is set in motion by turning the handle (F), which is fastened to an axis upon which are also a flywheel (G) and a pinion (I). The pinion works in a large cogwheel, which being connected with the cylinder causes its revolution upon the shaft (*a*). When steam power is available it is applied by means of the driving-wheels (H). When the kneading is completed the cover of the cylinder is raised by means of two cords, which are wound on two drums (M M') connected with a shaft (L) that is set in motion by a handle (J).

Fig. 570.



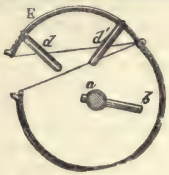


Fig. 571.

A similar machine, in which the arms do not stand opposite to the axis, but are bent spirally, has been constructed by Boland. It requires the application of somewhat more power than the preceding, but yields a dough more closely resembling that kneaded by hand.

Machine-made dough has the disadvantage of requiring a longer time to ferment than that kneaded by hand, but this may be overcome by the addition of a little more fresh or yeast, or increasing the quantity of sour dough. As a rule only half the finished dough is used in a baking, the other half being retained as ferment for the following batch.

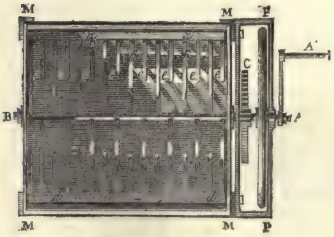


Fig. 572.

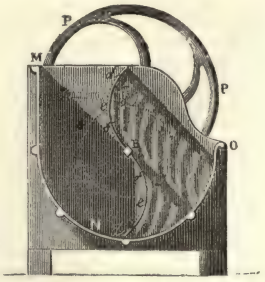


Fig. 573.

Rolland's kneading machine differs from the foregoing, as the trough is stationary whilst the kneading mechanism rotates. It is represented in horizontal section by fig. 572, and in vertical section by fig. 573. The trough (M M O) is semi-cylindrical, the side towards which the turning takes place being higher than the other, the trough

not being closed. The two end pieces (M M) are straight, and support the shaft (B) of the kneading machinery. This consists of an iron plate bent into the shape of an S (*d e f*), and several times divided, giving rise to a number of alternately long and short arms by which the kneading of the dough is effected. The apparatus is set in motion by the large cogwheel (C) working in a small one on the shaft (B), the power being applied through the handle (A′) and regulated by the flywheel.

Clayton's kneading trough, shown in section in fig. 574, consists of a cylinder (*a a*) into which the ingredients are put. It is mounted in a frame (*b*) with hollow axles

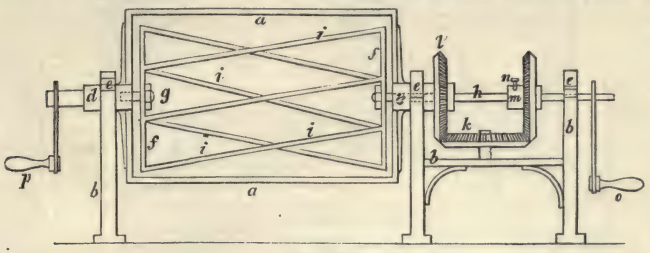


FIG. 574.

(*c d*), that turn in bearings at *e*. A revolving frame (*f*) supported in the interior of the cylinder by axles (*g h*). The ends of this revolving frame are braced together by oblique cutters or braces (*i i i*) that act upon the dough when the machine is put in motion, and effect the operation of kneading. The cylinder may be made to rotate without the internal frame, or the frame without the cylinder, or both may be made to revolve at the same time but in opposite directions; the respective motions being obtained through the gear work (*k l m*).

An American kneading machine consists essentially of a spiral arrangement, resembling a large corkscrew, working in a cylinder, by which the dough is worked up and finally pushed out well kneaded.

Perkins's hot-water oven is heated by means of pipes full of water, hermetically closed, but with sufficient space for expansion of the water within the pipes. The outer part is built of brickwork made very thick in order to retain the heat. The

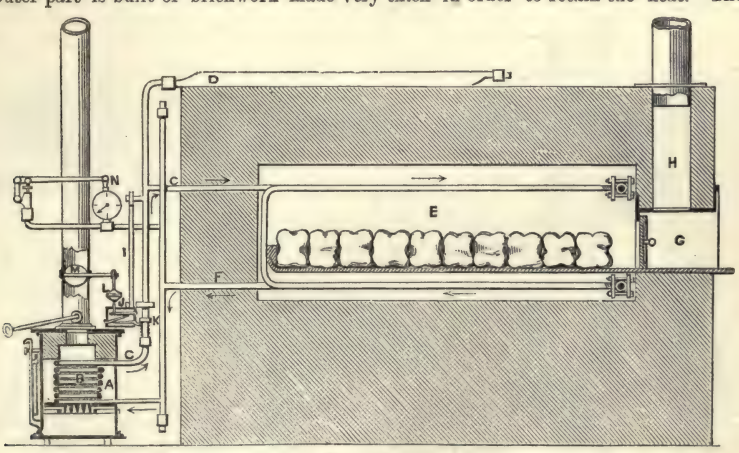


FIG. 575.

internal surface of the oven (E) is lined with wrought-iron pipes of 1 inch external and $\frac{5}{8}$th of an inch internal diameter, which are connected by the flow pipe (C C) with a coil of pipe (B) in the furnace (A); the coil has such a relative proportion of surface to that of the pipes in the oven as to allow of the temperature being raised to 288° and no higher. The temperature is maintained exactly constant by the expansion or contraction of a pipe (D) which acts upon three levers contained in the regulating box (J J), supported by the iron bar (I). The temperature is regulated by the adjustment of a movable nut (K) at the bottom of the expanding pipe. The least variation

in the temperature of the water in the pipes is sufficient to expand or contract the pipe (D), which at once acts upon the levers, and these raise or depress the straight rod (L) and open or close the damper (M) of the furnace. F is the return hot-water pipe; G, door of the oven; H, flue for the escape of vapour from the oven; N, an index of the temperature in the pipes.

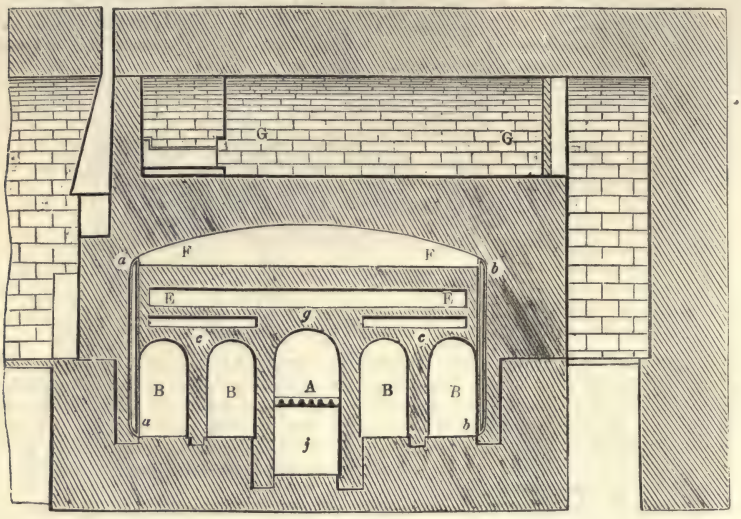


Fig. 576.

Grouvelle and Mouchot's oven.—This oven, which was originally constructed by Lemarre and Jamtel, but improved by Grouvelle and Mouchot, is shown in longitudinal and transverse section, by figs. 576 and 577. Coke or coal can be used

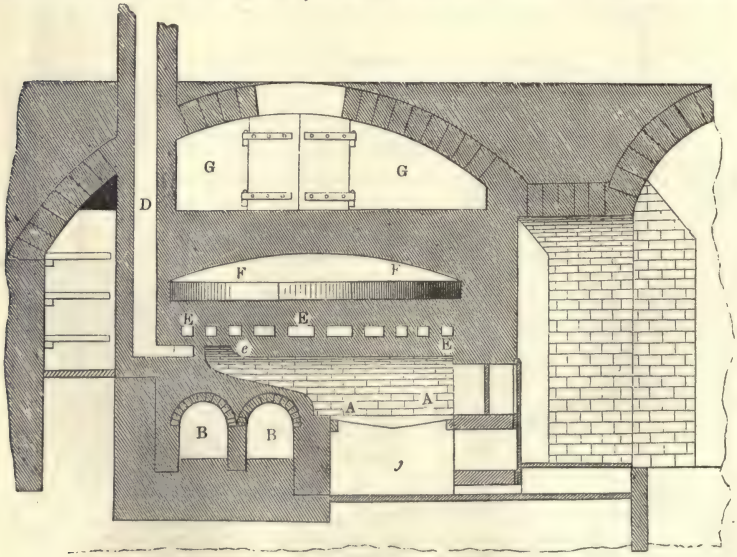


Fig. 577.

for the heating of this oven, and it is burnt in a fire grate (A) separate from the hearth. The oven is heated both by radiated heat and by currents of hot air. The baking hearth, with its arch, is shown at FF. The fire space (A) is divided in the middle by bars, so that the under portion (*j*) forms an ash-pit. The products of combustion

circulate in a series of flues (*c c*), imparting their heat to the sole of the oven, and finally passing into the chimney. During the baking the oven is entirely closed in order to keep up a regular circulation of the air. In proportion as the air in the oven becomes cooler, by parting with its heat, and specifically heavier, it sinks through a number of pipes (*b b*) into a system of arches (B B) distributed round the fire. After passing through these arches and becoming reheated, it passes upwards through *a a* and enters the flues (B B) immediately over the fire, where it is raised to the highest temperature, and then passes into the oven. The circulation is kept up continually, so that an incessant current of hot air flows into the oven. This oven presents the advantage of great cleanliness, as it yields a bread the crust of which is never contaminated by ash or cinders; it allows of the use of coal, which is cheaper than wood; finally, the operations can be carried on continuously, as the heat of the oven can be kept constant.

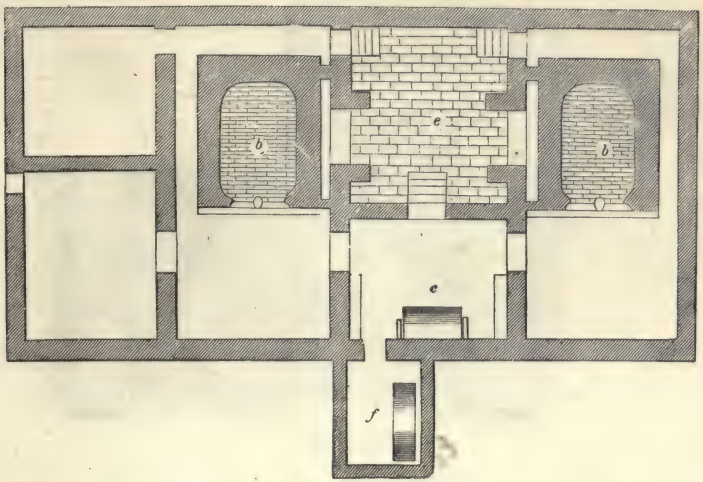


FIG. 578.

Fig. 578 represents a ground plan of a bakehouse in which such ovens are used: the ovens (*b b*) are separated by a space (*e*) common to the two ovens, into which the hot air passes. The kneading machine (*e*) is driven by machinery in the chamber (*f*).

Lespinasse's oven resembles the ordinary oven in which the heating material is burnt upon the hearth of the oven itself; but differs from it in the air draught not entering through the mouth of the oven, but through a flue lying under the hearth, so that only air already considerably heated enters the oven. The smoke also, instead of escaping through the mouth of the oven, passes into a chimney through a flue situated over the arch. This oven is usually heated with beech or poplar wood, or some other wood burning with a strong clear flame; oak and deal have, however, been used with advantage. About one-third of the cost of the combustibles can be recovered in the value of the charcoal produced. As soon as the oven has reached a temperature of about 200° this is withdrawn into closed vessels, where it is allowed to cool. The hearth is then cleansed, and the dough introduced.

Rolland's Oven.—The principle of this oven is essentially different from that of all others. The baking hearth is formed of iron plates supported upon an iron framework, and is covered with glazed tiles. It is not stationary, but can be revolved horizontally. In order to set the hearth in motion it is connected with a revolving shaft about 6 feet long, passing under the oven and having at its end a small conical cogwheel working in a spur wheel; the shaft is rotated by means of a handle. The shaft, and with it the hearth of the oven, can be raised or lowered at pleasure, the socket in which it rests being prolonged beneath into a screw worked by means of a lever. The heating is effected by passing the combustion products of a furnace into iron heating pipes situated under the movable hearth, and resting upon a bed of brickwork sloping slightly upwards from the furnace. The heating pipes open into vertical flues from which the hot air from the furnace is conducted into a compartment constructed of iron plates and situated above the baking space. The upper surface of this is covered with a layer of non-conducting materials, such as ashes; whilst from the under surface the heat radiates freely into the oven. The oven has therefore essen-

tially the construction of a muffle, all connection between the inner space and the heating space and the products of combustion being cut off.

The oven can be heated either with coal or wood. In the first case there is the fire space with its grate, and under this a roomy ash-pit. When wood is used the falling charcoal is caught in a charcoal extinguisher (B) placed under the fire space (fig. 579).

As the charcoal crumbles off from the burning wood it falls through the widely-placed bars of the grate into a shallow hopper (D), and from thence into the funnel-shaped head (C) of the extinguisher (B). This head is closed by a trap springing from

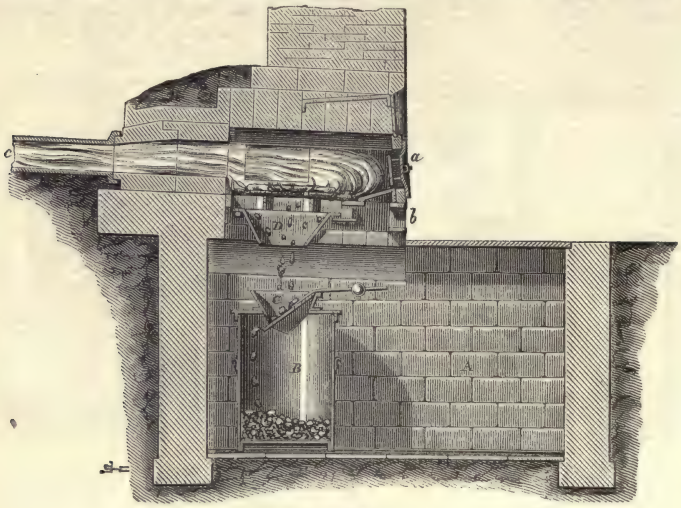


FIG. 579.

the inside and balanced by a weight. As soon as sufficient charcoal has collected in the head to overbalance this weight, the trap opens, allows the charcoal to fall into the extinguisher, and then closes again immediately, so that the glowing embers are preserved from contact with the air.

The introduction of the dough to be baked into the oven is easily effected. The portion of the hearth opposite the mouth of the oven (fig. 580) is first covered with loaves, and then by means of the handle (G) the hearth is rotated until the space opposite the mouth is again clear; this is in its turn covered with bread, and the operation is repeated until the hearth is full (fig. 581). The oven is emptied in a

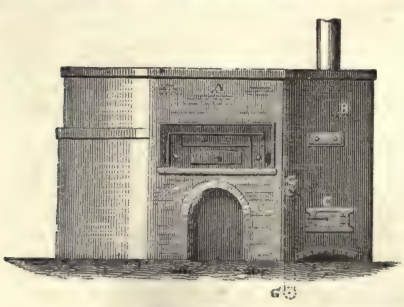


FIG. 580.

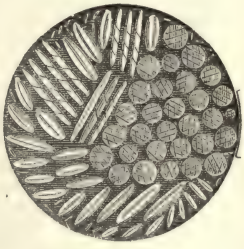


FIG. 581.

similar manner, the portion of the hearth first covered being, after the complete revolution, again opposite the mouth of the oven, so that the bread first put in presents itself first for removal. During the operation the progress of the baking can be observed through an opening covered with glass, the oven being lighted up with gas or otherwise; in the event of any irregularity of temperature becoming manifest, it can be overcome by rotation of the hearth.

Manufacture of Macaroni and Vermicelli.—The flour paste which comes into commerce under various forms and names is prepared from wheaten flour very rich in gluten by kneading it with comparatively little hot water, and pressing the stiff dough into shapes. The best vermicelli is made in Italy, from a hard wheat which is not ground to a fine flour, but worked as grit. 34 parts of grit are kneaded with 10 to 12 parts of boiling water into a perfectly homogeneous dough, and then pressed, the yield being about 30 parts of dry vermicelli.

In the manufacture of vermicelli, the gluten from the starch manufacture can be used with great advantage by adding it to flour poor in gluten. A product not inferior to the best Italian manufacture can be obtained by using 30 parts of ordinary flour, 10 parts of fresh gluten, and 5 to 6 parts of boiling water, the yield being about 30 parts. The vermicelli thus prepared is nourishing, and when boiled softens without dissolving.

In order to prepare a really white vermicelli, some manufacturers replace a portion of the flour by potato starch; but the improvement is only in the outer appearance, since, on account of the deficiency in gluten, the product is less nourishing and has the disadvantage of losing its consistency when boiled. By the addition of a corresponding quantity of wheat gluten, however, a good vermicelli can be prepared with potato flour.

According to Martin a good vermicelli can also be prepared from rice flour by the addition of wheat gluten; 50 parts of fresh gluten and 100 parts of rice flour being worked into a dough with 10 parts of boiling water.

In consequence of the necessary stiffness of the dough, the working of it cannot well be effected by hand or with the ordinary kneading machines. A special kneading stick is used, one end of which is fastened by a ring to the wall. With this kneading stick, which is shaped like a knife at one end for the purpose of cutting the dough and rounded at the other, the dough, after being prepared as far as possible by the hand, is worked until no further traces of flour are visible.

A machine for the working of this stiff dough is represented by fig. 582. It consists of a corrugated metal cylinder (A), which is rotated at the same time on its own

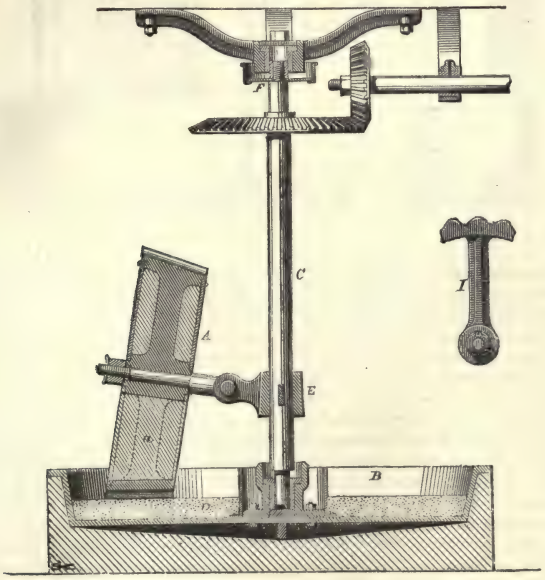


FIG. 582.

axis, and in a circular direction by the shaft (C), thus working up the dough (D) in the trough (B). It is useful to connect with the shaft (C) a shovel or plough, which follows the cylinder (A), and turns the dough after it has been pressed together. I is a front view of a segment of the cylinder, showing the corrugation. In the manufactory at Grenelle about 170 lbs. of flour and 5 gallons of water are mixed at each operation, and kneaded by such a machine into dough in 20 or 25 minutes.

The dough is shaped by means of presses shown in figs. 583 and 584, being introduced, still as hot as possible, into the bronze cylinder (D). It is then covered by a

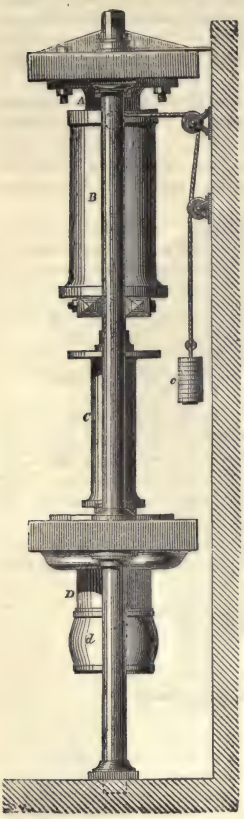


FIG. 583.

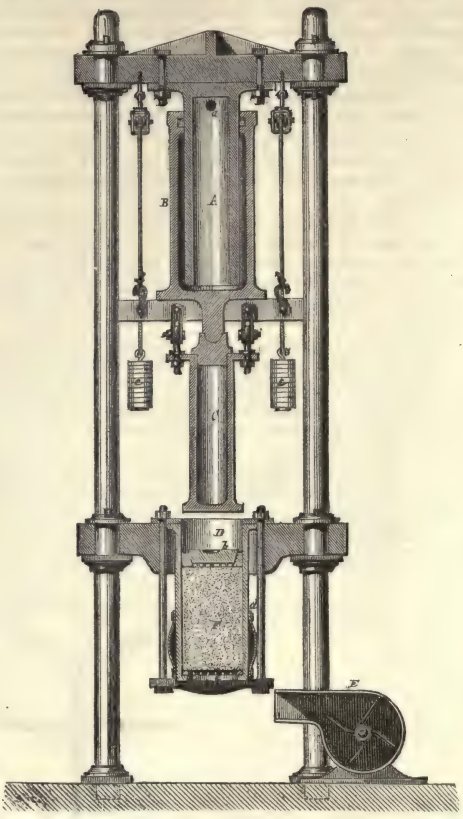


FIG. 584.

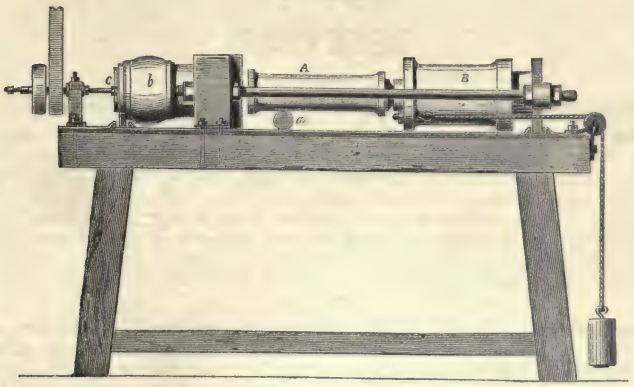
metal lid (B), and pressed out in the proper shape through the holes at the bottom, the pressure being applied by the piston (C) in connection with the hydraulic press (A B). To fill the pressing cylinder (D) the pump cylinder (B) is raised—after the emptying of the pump—by means of pulleys and balance weights (*c c*), the piston (C) is removed, and the dough introduced. The lower part of the pressing cylinder is surrounded by a jacket in which steam circulates in order to keep the dough hot during the pressing. The threads of vermicelli issuing from the cylinder are rapidly cooled on the surface by a powerful current of air issuing from the ventilator (E), which prevents them from adhering together. When they reach a length of about 3 feet they are cut off, laid upon screens, and carried into the drying room, where women cut the large pieces into smaller ones, roll them together, and place them on screens covered with paper in the drying oven.

For the preparation of macaroni the bottom plate is replaced by one having large circular openings provided with a mandril, which gives to the dough passing through the shape of a hollow pipe. The pipes are then hung on round rods and dried. In the preparation of macaroni, therefore, care must be taken to use a flour that will yield a dough sufficiently tenacious to bear this treatment, or the pipes will be broken through their own weight. These bottom plates are shown in figs. 586 and 587.

In the preparation of vermicelli moulded into different shapes—such as stars, crosses, wheels, rings, etc.—a similar press is used, but differing in being horizontal instead of upright. As shown in fig. 585 A is the pressing shaft, B the cylindrical hydraulic pump by which the shaft, supported by the roller (*a*), is driven forward into the filled pressing cylinder. In the bottom plate are openings corresponding to the

shape required. The thickness of the cake is regulated by a revolving knife which cuts the dough as it issues from the cylinder, the cakes being thicker or thinner according as the revolution of the knife is fast or slow. The cakes fall into a tray underneath, to which a movement to and fro is imparted in order to prevent the cakes from falling in one place and sticking together.

Fig. 585.



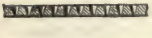


Fig 586.



Fig. 587.

A yellow colour is frequently given to the dough by mixing with it a small quantity of a decoction of turmeric or of saffron.

Granulated Gluten.—In some manufactories the greater part of the gluten from the starch manufacture is worked up into a kind of vermicelli, which comes into commerce under the name of granulated gluten. The fresh gluten, broken into small pieces, is kneaded into a stiff dough with double its weight of flour. The granulation of the dough is effected in a revolving cylinder, the inner surface of which is covered with iron spikes. Inside the cylinder is a stirrer, also provided with spikes, which revolves in the opposite direction. Both the cylinder and the stirrer make about fifty revolutions per minute. The granules thus obtained are dried in an oven and separated into different sizes by means of sieves of various degrees of fineness.

When prepared with the necessary care granulated gluten is preferable to the best vermicelli. It is more nourishing, being richer in gluten, has a pleasanter taste, does not boil down, but after about 5 minutes boiling becomes perfectly soft. Granulated gluten is particularly adapted for travellers in tropical countries and for use at sea; when properly packed it remains unaltered, whilst it is more nourishing than an equal volume or weight of flour or ship biscuit.

Alterations in Bread.—After keeping some time bread is subject to change through the formation of mould, the spores of which are brought into contact with it by the air. These develope with extraordinary rapidity into the well-known green and white mould spots, which quickly spread through the interior of the loaf and impart to it a disagreeable smell and taste. The development of this mould is more favoured in proportion to the moisture in the kneaded dough, and it takes place especially when the corn or flour has already suffered during production. Whether, as has been affirmed, the spores of the mould occur in the bread, having escaped the high temperature of the oven, appears doubtful; it is much more probable that bread prepared from altered flour presents a specially favourable soil for the development of mould; and that bread prepared from good flour does not favour the germination of the falling spores to the same extent. The best protection against mould is to avoid an excess of water in the bread crumb and to use a larger addition of salt; but especially a rapid consumption. Less frequently, a red fungus, the *Oidium aurantiacum*, makes its appearance in bread, to which it imparts all the injurious properties of the ordinary mould.

DEXTRIN.

Occurrence.—Dextrin is widely distributed in the sap of various plants.

Characters.—Dextrin is soluble in water and dilute alcohol, but insoluble in strong alcohol. It has the same percentage composition as starch and cellulose. When quite pure dextrin is not coloured by iodine, and the brownish red coloration, sometimes observed upon treating solutions of dextrin with iodine, is due according to Payen to the presence of unaltered starch. Dextrin resembles in many respects gum; consequently it can be employed for many purposes in the place of gum, and this fact has led to its production on a large scale. Dextrin and gum are, however, chemically different; the former does not yield mucic acid by oxidation with nitric acid.

Preparation.—Chemically pure dextrin is prepared by heating starch with dilute hydrochloric acid, until the liquid when treated with a solution of iodine assumes a claret colour. The cooled liquid is then treated with strong alcohol until a flocculent precipitate begins to be deposited. This flocculent precipitate contains the unchanged starch, which is not soluble in alcohol and is filtered off. To the clear filtrate alcohol is again added until the precipitate formed ceases to increase upon further addition of alcohol. The precipitated dextrin is then filtered off and washed with alcohol upon a filter to remove grape sugar. Dextrin thus prepared is, however, still not quite pure; it requires to be again dissolved in water, precipitated and washed with alcohol, this operation being repeated several times until a product is obtained which does not reduce an alkaline solution of cupric oxide. On the large scale dextrin is generally obtained either by heating starch or by treating it with dilute acids. As obtained by the former method, dextrin is always yellow or brown in colour, while it may be obtained almost colourless by the latter method.

In preparing dextrin by roasting starch, an oven is employed capable of being heated by hot air. The dry starch is exposed to heat in thin layers in trays. The air is heated by passing through flues before entering the oven. The starch gradually becomes yellowish brown, and is converted into dextrin, which is for the most part soluble in water.

The regulation of the temperature in this operation is somewhat difficult, and therefore some manufactories employ a copper cylinder placed in an oil bath, which is kept at a constant temperature of 210°. The starch is placed in the cylinder, which is furnished with a stirrer, so as to continually bring fresh portions of starch in contact with the heated surface. By this means starch is converted more completely and rapidly into dextrin than in the oven above described.

By treating starch with a very small quantity of acid, nitric acid being best for the purpose, its conversion into dextrin is effected much more easily at a low temperature, a white, friable, and very soluble product being obtained. For this purpose Payen recommends the following procedure: 2 lbs. of nitric acid, sp. gr. 1·310 to 1·360, are mixed with 300 lbs. of water and 1,000 lbs. of starch, the whole being carefully mixed and dried in the open air. As soon as the mass is dry enough to admit of being broken in pieces, it is beaten into cakes, from 4 to 5 inches thick, with a flat instrument, and heated in the shallow brass boxes above described. The conversion of the starch into dextrin takes place at a temperature between 110° and 120° within 2½ hours. When the temperature of the oven does not exceed 100°, 4 hours are necessary; at a temperature of 130° the conversion is complete in 30 or 40 minutes.

When the conversion of the starch is complete, the boxes are emptied into shallow brickwork vessels, where the dextrin cools and is then ready for the market. It is packed in well-dried casks, secured with iron bands, and lined internally with paper saturated with turpentine so as to keep out dust.

Dextrin prepared by treating starch with acid is pulverulent and has the appearance of starch; it is almost as white when the temperature has not been high. A still better and whiter product is obtained by using hydrochloric instead of nitric acid. For this purpose 500 lbs. of starch are moistened with a mixture of 1 lb. hydrochloric

acid and 125 lbs. of water. The mixture is kept in an oven at a temperature between 55° and 60° for 48 hours, in order to dry it completely; and then it is heated for 4 hours to a temperature of 110° or 120°. In this case zinc boxes are used.

White dextrin is also obtained by using sulphuric acid. The acid is diluted with water in the same proportions as above, and is most conveniently mixed with the starch in a kneading machine. In using sulphuric acid the temperature need not exceed 45° or 50°. The boxes in which the mixture is placed in the oven may in this case be made of iron. The conversion of the starch and the solubility of the product obtained is in proportion to the amount of acid employed.

Dextrin may be obtained in the wet way by using diastase or malt extract; the product thus obtained always contains some sugar. For many purposes dextrin containing sugar is preferable.

To prepare dextrin by means of diastase, an infusion of malt is heated to 75° and mixed with starch as long as this is dissolved, the temperature of the mixture being maintained meanwhile by passing into it a sufficient quantity of steam. The point of complete change of the starch is ascertained by means of iodine, for which purpose a small quantity of the liquid is treated with a drop of aqueous solution of iodine. So long as a blue coloration is observed, unaltered starch is present; but when the liquid assumes a claret colour the further action of diastase must be stopped. This is done by blowing steam into the liquid, and bringing it quickly to the boiling point. Prolonged action of diastase would give rise to the production of a material too rich in sugar. Directly the liquid begins to boil the further action of the diastase stops, and the boiling liquid is run off through a filter into a reservoir and concentrated until it assumes a viscous consistency. This kind of dextrin is used in some breweries. This dextrin syrup is stated by Payen to contain 52·71 per cent. of grape sugar and 47·29 per cent. of dextrin.

Dextrin syrup may be also prepared by acting upon starch with dilute acids, such as sulphuric acid. The acid liquid obtained is saturated with chalk, the precipitate of gypsum filtered off, and the filtrate concentrated. The greater part of the gypsum which still remains in fine suspension separates during the concentration, and the filtered liquid is concentrated to the proper strength.

The syrup thus obtained is colourless, but has the disadvantage that it contains calcium sulphate. For this reason brewers prefer dextrin syrup prepared with malt to that prepared with sulphuric acid.

The methods described for the preparation of dextrin yield products pure enough for industrial purposes, although the dextrin prepared in the dry way always contains a certain amount of unchanged starch, and that prepared in the wet way always contains grape sugar.

Uses.—Dextrin is used in confectionery, as weaver's dressing, for making mucilaginous drinks, in the manufacture of beer, fruit wines, brandy, liqueurs, court plaster, etc. In the form of British gum, either alone or together with starch, it is used for finishing bobbin-net and fine fabrics, and as weaver's dressing, in which case it is sometimes mixed with glycerin; it is also used for thickening mordants in dyeing and calico printing, and for rendering envelopes, postage stamps, etc., adhesive. Dextrin in the form of powder has been used by Velpeau with great success in the place of paste bandages for fractured limbs. For this purpose it is stirred with some camphorated spirit, and the whole mixed with 40 per cent. of lukewarm water. The dextrin absorbs the water and speedily dissolves to a thick liquid, which is then spread upon linen. The bandages are at once laid upon the part to be protected, and when dry they afford a complete protection against dislocation of the fracture.

SUGAR.

Under the name sugar are included a number of substances characterised by sweet taste, and presenting several other features of analogy physically as well as chemically. An intimate relation exists between various kinds of sugar and starch, cane sugar being to a certain extent intermediate between starch and grape sugar, containing more water than starch, and less than grape sugar, as shown by the following comparison:—

Starch	$2C_6H_{10}O_5 = C_{12}H_{20}O_{10}$
Cane sugar	$C_{12}H_{22}O_{11}$
Grape sugar	$2C_6H_{12}O_6 = C_{12}H_{24}O_{12}$

Starch is readily convertible into grape sugar with the assimilation of water, and cane sugar is convertible into grape sugar, also with the assimilation of the elements of water. By the action of diastase upon starch a variety of sugar called maltose is produced, which has a composition the same as that of lactose.

Occurrence.—The different kinds of sugar are very widely distributed in the vegetable kingdom; and probably there is no plant which does not contain one or other kind of sugar. A particular kind of sugar occurs in milk, and under special conditions sugar occurs in other animal secretions. The kinds of sugar most frequently occurring are: glucose, $C_6H_{12}O_6$, comprising grape sugar and fruit sugar; saccharose, or cane sugar, $C_{12}H_{22}O_{11}$; and lactose, or milk sugar, $C_{12}H_{22}O_{11}.H_2O$. These kinds of sugar are compounds of carbon with hydrogen and oxygen in the same proportions as in water. They may be regarded as derivatives of a hexatomic alcohol, $C_6H_{14}O_6$. Among other kinds of sugar of similar composition are inosite, $C_6H_{12}O_6$, occurring in the unripe fruit of *Phaseolus vulgaris*, in other plants, and in the animal organism; sorbin, having the same composition, occurs in the berries of the mountain ash, *Sorbus Aucuparia*; melitose, having the same composition as cane sugar, occurs in various species of *Eucalyptus*. In addition to these, some other kinds of sugar occur, having a somewhat different composition. For example, mannite, $C_6H_{14}O_6$, the chief constituent of manna, an exudation from *Fraxinus ornus*, occurs also in other plants, in seaweed, and in mushrooms. Substances closely analogous to the last named occur in *Melampyrum nemorosum*, in the berries of the mountain ash, and in a Californian pine, *Pinus Lambertiana*.

Glucose. This variety of sugar is present in most sweet-tasting fruits, and in many other parts of plants in various proportions, as follows:—

Strawberry (Princess Royal)	5·86 per cent.
Cherry	10· ,,
Fresh grapes from Fontainebleau	9·42 ,,
Preserved grapes	16·5 ,,
Hot-house grapes	18·37 ,,
Green grapes	1·60 ,,
White currant	6·40 ,,
Green figs	11·55 ,,

But there are at least two different kinds of glucose, distinguishable chiefly by their relation to polarised light. One kind is crystallisable, and on account of the large amount contained in grape juice, it is often called grape sugar. It turns the plane of polarisation to the right, and is for that reason termed dextrose. This kind of sugar sometimes occurs also in animals, and in the disease termed diabetes, large quantities of it are excreted in the urine. The other kind is uncrystallisable, and as it turns the plane of polarisation to the left, it is called laevulose; honey consists chiefly of this sugar. According to the source from which these kinds of sugar are obtained, a numbers of distinctions were formerly made which are now no longer recognised.

Glucose also occurs very frequently in a state of combination, constituting a variety of substances known as glucosides which are decomposed by boiling with

dilute acids or alkalies and by the action of ferments, yielding glucose and other substances. Amongst the more important of the substances of this class are amygdalin ($C_{20}H_{27}NO_{11}$), salicin ($C_{13}H_{18}O_7$), æsculin ($C_{21}H_{24}O_{13}$), glycyrrhizin ($C_{24}H_{36}O_9$), and arbutin ($C_{12}H_{16}O_7$).

Saccharose or cane sugar occurs in the juice of the *Saccharum officinarum* or sugar cane; it also occurs abundantly in the sugar grass (*Sorghum saccharatum*), in maize, beetroot, melons, the cocoa nut, in pine apples, in chestnuts, in the juice of palms, in the sugar maple, and in the bulbs of many liliaceous plants. At one time it was supposed that the parts of plants, the juice of which had an acid reaction, contained no cane sugar, since this substance is easily converted by the action of acid into a mixture of grape sugar and fruit sugar. However, the researches of Payen and Buignet have shown that even the most acid fruits may contain abundance of cane sugar.

Payen showed that the juice of oranges and of lemons contains cane sugar; and Buignet found in various fruits the following amounts of cane sugar and other kinds of sugar:—

	Cane Sugar	Total Sugar
	per cent.	per cent.
Pineapple (Montserrat)	11·33	13·30
Strawberry (Collina. d'Ehrhardt)	6·33	11·31
Apricot	6·04	8·78
Apple, grey Reinette, fresh	5·28	14·00
„ „ „ preserved	3·20	15·83
„ English	2·19	7·65
„ Calville, preserved	0·43	6·25
Plum, Mirabelle	5·24	8·67
„ Reine Claude	1·23	5·55
Orange	4·22	8·58
Lemon	0·41	1·47
Raspberry	2·01	7·23
Peach	0·92	1·99
Pear, St. Germaine, preserved	0·36	8·78
Pear	0·68	7·84

Characters.—Of those kinds of sugar which are frequently met with, cane sugar is the most easily crystallisable; grape sugar crystallises only with difficulty, and fruit sugar not at all.

Glucose or grape sugar is considerably less sweet than cane sugar, three times as much being necessary to produce the sweetness due to a given quantity of cane sugar. Glucose crystallises from its aqueous solutions, taking up a molecule of water, in which state its composition may be represented by the formula:

$$C_6H_{12}O_6 + H_2O.$$

When heated up to 100° it melts, giving up its water of crystallisation, differing in this respect from cane sugar, which contains no water of crystallisation. Anhydrous grape sugar exposed to a moist atmosphere slowly absorbs water of crystallisation. Grape sugar is more soluble in alcohol than cane sugar: 100 parts of boiling alcohol dissolve 1·66 parts of grape sugar; alcohol of 83 per cent. dissolves 18 parts of grape sugar. At a high temperature grape sugar is converted into glucosan, caramel, and other brown substances.

The alkalies and alkaline earths combine with grape sugar. These compounds are, however, very unstable even at the ordinary temperature, and the solutions are instantly decomposed upon heating; they begin to colour at 70°, and when heated to boiling in contact with atmospheric air they become at once black. By the action of alkalies upon grape sugar a body called glucinic acid, $C_{12}H_{16}O_9$, is formed, besides other substances. The deportment of alkalies towards grape sugar admits of its presence being detected even in small proportion when mixed with cane sugar. Since cane sugar is not affected in the same manner by alkalies no colouration is obtained by boiling solutions of pure cane sugar with alkalies.

Concentrated sulphuric acid dissolves grape sugar, forming with it gluco-sulphuric acid, which yields soluble barium and calcium salts. Protracted boiling with dilute sulphuric or hydrochloric acids renders grape sugar unfermentable, it is then gradually changed into dark coloured substances, caramel, etc. Cupric oxide in alkaline solution is reduced by grape sugar to cuprous oxide. Solutions of grape

sugar are decomposed by yeast, yielding alcohol and carbonic dioxide besides other products, the formation of alcohol taking place according to the following equation:

$$C_6H_{12}O_6 = 2CO_2 + 2C_2H_6O.$$

(See FERMENTATION.)

Grape sugar turns the plane of a polarised ray of light to the right, fruit sugar turns it to the left.

The behaviour exhibited by grape sugar towards alkaline solutions of cupric oxide is taken advantage of in determining grape sugar quantitatively. For this purpose it is only necessary to know how much of a saccharine liquid is required for the complete precipitation of the copper in a solution of cupric oxide of known strength; 1 molecule of grape sugar reduces 10 molecules of the cupric salt to cuprous oxide, or in other words 5 grammes of grape sugar decompose 34·64 grammes of crystallised cupric sulphate. The cupric oxide solution is prepared in these proportions by dissolving 34·64 grammes of pure cupric sulphate in 150 or 160 c.c. of water; adding 150 grammes of crystallised potassium tartrate dissolved in 600 or 700 c.c. of a solution of sodium hydrate. At first there is formed a voluminous light blue precipitate which dissolves upon shaking, forming a dark blue liquid, which is then diluted with water to the volume of 1,000 c.c. The solution thus prepared is preserved for use in a dark place.

In applying the test 1 gramme of the saccharine substance is placed in a flask holding 100 c.c. dissolved in water and the solution diluted exactly to 100 c.c. A measured quantity (20 c.c.) of the solution of cupric oxide is then diluted with twice or thrice its volume of water and heated to boiling in a porcelain dish. The blue liquid must remain perfectly clear during this operation. Should the liquid have been kept so long that cuprous oxide is precipitated upon simply boiling, it is then worthless and a fresh solution must be prepared. Some of the sugar solution is then dropped from a burette into the hot liquid in the porcelain dish, observing after each addition whether the copper solution still appears there; so soon as this ceases to be the case it is a sign that all the cupric oxide is reduced and the experiment is complete. It is advisable to repeat the experiment, the second time adding approximately as much sugar solution as in the first experiment, and then to proceed very carefully with the conclusion of the operation. Thus, for instance, should the copper solution in the first experiment remain palpably blue after adding 11 c.c. of sugar solution, but become colourless upon the addition of another cubic centimetre, then in performing the operation a second time, 11 c.c. of sugar solution may be at once added.

Since 1,000 c.c. of copper solution contain exactly as much cupric oxide as 5 grammes of pure grape sugar are capable of reducing, it follows that the 20 c.c. would in the testing represent exactly 0·100 gramme of grape sugar. If, therefore, the liquid to be tested has been diluted to 100 c.c., and 11·6 c.c. taken for the test, the percentage of grape sugar in it is found by the simple proportion

$$11{\cdot}6 : 0{\cdot}100 = 100 : x; \; x = 0{\cdot}862.$$

Saccharose or cane sugar crystallises in rhomboidal prisms. When deposited from a hot concentrated solution, quickly cooled, the crystals are small and adhere together, forming a granular mass; by allowing the warm solution to evaporate very slowly, very large crystals are formed (sugar candy).

Cane sugar has a specific gravity of 1·606. When rubbed or struck in the dark, it emits a phosphorescent light; by long continued trituration, cane sugar undergoes alteration and acquires a peculiar smell.

Cane sugar is very soluble in water, one-third of its weight of water being sufficient to dissolve it in the cold, and in boiling water it is soluble in almost any proportion. The boiling point of a solution of sugar varies with the amount of sugar present, rising in proportion as the syrup contains less water. If the heat be continued, the sugar remaining after evaporation melts at a temperature only a little above the boiling point of the saturated solution. When the boiling point of a cane sugar solution is lowered very considerably by evaporating under reduced pressure, a very copious crystallisation of the sugar takes place in the boiling solution.

Solution of cane sugar possesses the property of rotating the plane of polarisation of a ray of light to the right, the specific capacity of rotation being: D = 73·8°. Cane sugar is insoluble in cold absolute alcohol, but boiling absolute alcohol dissolves 1·25 per cent. of cane sugar, which is again almost completely deposited upon cooling; alcohol of 83 per cent. dissolves 25 per cent. of cane sugar. When a cold saturated solution of cane sugar in 90 per cent. alcohol is mixed with double its volume of ether, the sugar is precipitated in the form of minute crystals on the sides of the vessel containing the solution. This reaction may be used for determining the presence of cane sugar in different parts of plants; the juice or an aqueous extract of the plant is evaporated to dryness at a low temperature, then treated with alcohol, the insoluble

portion separated by filtration, and the solution mixed with ether; any cane sugar present crystallises out after a short time.

Cane sugar combines with a number of bases, such as lime, baryta, lead oxide, potash and soda. These compounds have been carefully studied by Peligot and Soubeiran. A large quantity of calcium hydrate is dissolved when heated with a solution of cane sugar. The solution prepared in the cold, provided the concentration of the liquid does not exceed a certain limit, is a compound of 1 molecule of sugar with 1 molecule of calcium oxide:

$$C_{12}H_{22}O_{11}.CaO.$$

In concentrated solution of sugar, lime is dissolved in greater proportion. If such a solution be heated to boiling it becomes cloudy, and a bulky precipitate is formed which may be separated by filtering the hot liquid, and purified by washing with boiling water. This insoluble compound consists of 1 molecule of cane sugar and 3 molecules of lime:

$$C_{12}H_{22}O_{11}.3CaO.$$

It is formed by the decomposition of 3 molecules of the first mentioned compound, 1 molecule of the tribasic compound being produced, while 2 molecules of sugar are set free:

$$3(C_{12}H_{22}O_{11}CaO) = C_{12}H_{22}O_{11}.3CaO + 2(C_{12}H_{22}O_{11}).$$

If the precipitate be suffered to cool in the liquid from which it was formed, it redissolves and the first compound is again produced. The monobasic compound may be prepared in a pure state by digesting lime with a tolerably concentrated solution of sugar until no more lime is dissolved; the liquid is then filtered, mixed with a small quantity of sugar in order to convert all the sugar lime into a monobasic compound, and alcohol added; a dirty white precipitate is formed which is insoluble in alcohol, and after the removal of the liquid forms an amorphous brittle mass. The substance thus prepared behaves exactly like a solution of lime in sugar: it is completely soluble in water, and is decomposed when heated, etc.

Upon mixing a solution of the monobasic lime compound with a second molecule of sugar, and then with hydrated cupric oxide, the latter is dissolved. The same liquid in contact with metallic coppper and atmospheric oxygen causes oxidation of the metal, and the cupric oxide is dissolved. The proportion of lime taken up by a solution of sugar varies very much according to the concentration of the sugar solution. Very concentrated solutions of sugar take up as much as 2 molecules of lime to every molecule of sugar, while dilute solutions take up less than 1 molecule.

The following table by Peligot shows the relative proportions of sugar and lime in solutions of different degrees of concentration, and also the specific gravity of the solutions; for the sake of comparison the proportions of sugar and lime in the compounds, containing respectively 1 and 2 molecules of lime, are given; the latter compound however is not known in the pure state.

Percentage of sugar	Specific gravity		100 parts of sugar lime contain	
	of sugar solution	of sugar solution saturated with lime	Lime	Sugar
$C_{12}H_{22}O_{11}.CaO$	—	—	14·1	85·9
$C_{12}H_{22}O_{11}.2CaO$	—	—	24·7	75·3
40·0	1·122	1·179	21·0	79·0
37·5	1·116	1·175	20·8	79·2
35·0	1·110	1·166	20·5	79·5
32·5	1·103	1·159	20·3	79·7
30·0	1·096	1·148	20·1	79·9
27·5	1·089	1·139	19·9	80·1
25·0	1·082	1·128	19·8	80·2
22·5	1·075	1·116	19·3	80·7
20·0	1·068	1·104	18·8	81·2
17·5	1·060	1·092	18·7	81·3
15·0	1·052	1·080	18·5	81·5
12·5	1·044	1·067	18·3	81·7
10·0	1·036	1·053	18·1	81·9
7·5	1·027	1·040	16·9	83·1
5·0	1·018	1·026	15·3	84·7
2·5	1·009	1·014	13·8	86·2

The solubility of lime in dilute solution of sugar was studied by Berthelot. The following table gives the results of his researches. Columns I. and II. show the percentage amounts of sugar and lime in the solution. Column III. shows the ratio of sugar to lime; but since the ratio is somewhat obscured in dilute solutions because pure water dissolves some lime, Column IV. gives the ratio of sugar to lime after making allowance for the lime dissolved in water alone. The numbers show that the monobasic compound was only formed in the first experiment, while in every other case, owing to the small amount of sugar, the proportion of lime dissolved was less than 1 molecule of lime for each molecule of sugar.

I.	II.	III.		IV.	
Sugar	Lime	Lime	Sugar	Lime	Sugar
4·850	1·301	17·5	82·5	15·4	84·6
2·401	0·484	16·8	83·2	12·3	87·7
2·000	0·433	17·8	82·2	12·5	87·5
1·660	0·364	18·0	82·0	11·5	88·5
1·386	0·326	19·0	81·0	11·4	88·6
1·200	0·316	20·8	79·2	12·2	87·8
1·058	0·281	21·0	79·0	11·2	88·8
0·960	0·264	21·6	78·4	10·8	89·2
0·400	0·194	32·7	67·3	10·3	89·7
0·191	0·172	47·4	52·6	11·2	88·8
0·096	0·154	61·6	38·4		

Not only in respect to the solubility of the lime, but also when heated, the liquids behave differently, according to their strength. Coagulable sugar lime is obtained by mixing a solution of 25 parts of sugar in 50 parts water with 51 parts dry lime suspended in 50 parts of water, stirring the mixture for about ten minutes, then adding 3 parts more lime, again stirring, and finally filtering, after having allowed the mixture to stand for half an hour. The clear filtrate coagulates when it is slowly heated to boiling, and becomes clear again upon cooling. When, however, it is heated very quickly to boiling and a lively ebullition is kept up, no coagulation takes place. Upon diluting the liquid with 2, 3, and 4 times its bulk of water, a milky cloudiness is produced upon boiling, and the liquid is no longer transparent or translucent, but it does not coagulate. A solution which does not coagulate when heated to boiling is obtained by using less water. Upon mixing lime and sugar in the above proportions with only one half the quantity of water, the solution may be heated slowly or quickly without coagulating. Protracted contact with the air causes the formation of an opaque pellicle of calcium carbonate upon the surface of the liquid.

Sugar lime is easily decomposed by all acids, even carbonic acid. Upon mixing concentrated solutions of caustic baryta and cane sugar, a crystalline paste is formed, and the same compound is formed upon boiling dilute solutions. It has a composition analogous to that of the monobasic lime compound, $C_{12}H_{22}O_{11}.BaO$. Upon mixing an alcoholic solution of cane sugar with potash or soda, a sticky precipitate is formed, which hardens in alcohol; the potassium compound is represented by the formula: $C_{12}H_{22}O_{11}.K_2O$.

Another compound is obtained by treating sugar lime with lead acetate, or by mixing concentrated solutions of sugar with an ammoniacal solution of lead acetate. A gelatinous precipitate is formed, which dissolves in boiling water, and after a while deposits acicular crystals. The composition of this substance differs from that of the other compounds, the lead oxide replacing 2 molecules of water, as shown in the following formula: $C_{12}H_{18}Pb_2O_{11}$ or $C_{12}H_{18}O_9.2PbO$.

Cane sugar differs from grape sugar in its behaviour towards alkaline bases. Grape sugar when treated with alkalies or alkaline earths decomposes slowly at the ordinary temperature, but immediately upon boiling, with the formation of brown or black products; while cane sugar combines with these reagents without decomposition. Use is made of this different behaviour of these two sugars in distinguishing them in analytical chemistry. Besides entering into combination with bases, cane sugar also forms compounds with certain salts—for instance, with sodium chloride or common salt. The composition of the compound is represented by the formula: $C_{12}H_{22}O_{11}.NaCl$; or according to other analyses: $C_{12}H_{22}O_{11} + C_{12}H_{20}O_{10}.2NaCl$.

The compound of sugar with sodium chloride is even more soluble in water than pure sugar; upon evaporating solutions of sugar containing sodium chloride, this compound remains dissolved after the excess of sugar has crystallised out. For this

reason the presence of sodium chloride in the juice of sugar cane or beet root is very disadvantageous, since a part of the sugar is thus rendered uncrystallisable and retained in the molasses. From the formula of the compound it will be seen that the sodium chloride is combined with nearly six times its weight of sugar, and that hence the production of sugar from beet grown on a salt soil would be attended with great disadvantage and loss. A sugar factory established near Naples was ruined from this cause; the beets having been grown on a soil situated near the sea, were impregnated with salt, and they contained so much sodium chloride that the juice yielded no crystallisable sugar at all. The chlorides of ammonium and potassium enter into similar combination with sugar.

Cane sugar melts at 160°, and upon cooling solidifies to a transparent amorphous mass called **barley sugar**, which gradually becomes opaque and crystalline. Upon heating cane sugar for some time at a temperature of 170°–180°, according to Gélis it is converted into a mixture of equal molecules of grape sugar and of a substance having the same constitution as starch and cellulose, which he called **saccharid** or **glucosan**. This change may be considered as consisting in the removal of a molecule of water from one molecule of cane sugar, and its transfer to another to form grape sugar: $2C_{12}H_{22}O_{11} = 2C_6H_{12}O_6 + 2C_6H_{10}O_5$.

An aqueous solution of melted cane sugar treated with yeast yields only half the quantity of alcohol and carbonic acid obtainable from ordinary cane sugar. The solution of melted sugar reduces alkaline solutions of cupric oxide, but it yields only one half as much cuprous oxide as is obtained when cane sugar has been converted by an acid into grape sugar and fruit sugar. This shows that by melting cane sugar one half of it is converted into a fermentable substance, capable of reducing cupric oxide (grape sugar), while the other half is converted into a non-fermentable substance which does not reduce cupric oxide (saccharid).

By protracted heating at a temperature of 180°–200° cane sugar assumes a yellow colour which passes into different shades of brown, and finally, with evolution of water and inflammable products, the sugar is converted into a mixture of substances known under the name of **caramel**. According to Gélis, caramel consists of three distinct substances, the relative proportions of which depend upon the temperature and the duration of the heating. The first product formed appears to be caramelan $C_{12}H_{18}O_9$, which under evolution of water passes into caramelene and caramelin. All three substances combine with bases. Caramel is soluble in water and in alcohol, and under the name of **couleur** is used for colouring liqueurs and for various culinary purposes.

When strongly heated cane sugar swells up, gives off a number of inflammable products, and finally yields a voluminous and difficultly combustible charcoal.

Aqueous solutions of cane sugar are changed by protracted boiling, a part of the sugar becoming uncrystallisable.

Cane sugar is not itself fermentable, but in contact with yeast it undergoes alteration; and taking up the elements of water, it is converted into a mixture of equal molecules of grape sugar and fruit sugar, which are both fermentable. This change may be represented by the following equation:

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Grape sugar}}{C_6H_{12}O_6} + \underset{\text{Fruit sugar}}{C_6H_{12}O_6}$$

The same change takes place when a solution of cane sugar is heated for a short time with a trace of free acid. The mixture of the two kinds of sugar turns the plane of polarised light to the left, for which reason sugar that has been altered by acids is called **inverted sugar**. Since the formation of inverted sugar reduces the quantity of crystallisable sugar, the sugar manufacturer takes care to keep the juice operated upon continually alkaline with small quantities of sugar lime during the entire operation.

Concentrated acids decompose cane sugar; treatment with hydrochloric or sulphuric acid, and the application of a gentle heat, produce humus substances, which become continually richer in carbon as the reaction proceeds. Concentrated nitric acid changes cane sugar into nitro-saccharose, a substance resembling gun cotton in its properties. When sugar is heated for a short time with nitric acid of specific gravity 1·310, a deliquescent acid—saccharic acid—is produced; and, by protracted boiling with nitric acid, oxalic acid is formed.

Lactose, or milk sugar ($C_{12}H_{22}O_{11}\cdot H_2O$) is much less soluble than either grape or cane sugar, requiring five or six times its weight of cold water for solution. It is not so sweet as grape sugar and is dextro-rotatory. It crystallises in hard white, translucent, four-sided prisms. Lactose combines with bases, forming compounds that have an alkaline reaction, and by the action of dilute acids it is converted into galactose ($C_6H_{12}O_6$), a readily crystallisable dextro-rotatory glucose, distinguished by yielding mucic acid ($C_6H_{10}O_8$), when oxidised by the action of nitric acid, instead of saccharic acid ($C_6H_{10}O_8$).

Milk sugar does not readily undergo alcoholic fermentation. When decomposing gluten or casein is used as the ferment, milk sugar is chiefly converted into lactic acid ($C_3H_6O_3$), but some alcohol is formed at the same time.

Preparation.—The kind of glucose commonly known as grape sugar or dextrose is produced by the protracted action of dilute acids or diastase upon starch, and also by the decomposition of a number of organic substances termed glucosides; thus, for instance, amygdalin can be decomposed into grape sugar, oil of bitter almonds, and hydrocyanic acid:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + CNH + 2C_6H_{12}O_6.$$

The glucose obtained from these sources sometimes presents peculiarities and differs in the facility with which it undergoes alcoholic fermentation. Cellulose is also convertible into ordinary glucose by the action of dilute acids.

Grape sugar is artificially prepared from starch, which is converted into grape sugar by addition of the elements of two molecules of water. It may also be prepared from cane sugar, and is met with in commerce in three different conditions, as hard sugar, granular sugar, and as syrup.

The manufacture of grape sugar from starch is carried out by heating a mixture of starch with dilute sulphuric acid, by forcing steam into the liquid contained in large wooden vats in which about 1,000 gallons of water and 84 lbs. of sulphuric acid are first mixed, and heated to boiling. Meanwhile about 2 cwts. of starch are mixed with 30 gallons of lukewarm water in a smaller vat. The liquid in the large vat is kept boiling, and the mixture of starch and water is run in until about 4,000 lbs. of starch and 600 gallons of water have been added. After adding the last portion of starch and water the liquid in the vat is kept boiling about 40 minutes, and then a few drops are taken out and tested with a drop of iodine solution, which ought not to produce any blue coloration; if it does, the boiling is continued and the liquid tested with iodine solution from time to time until no coloration is produced. When this point has been reached, the steam is shut off and the liquid neutralised with chalk, previously powdered and stirred up with water to a thin pap, which is added in small quantities at a time until no effervescence is observed upon the addition of a fresh portion, or, what is still better, until a drop of the liquid ceases to colour blue litmus paper red. A large excess of chalk is avoided, owing to its rendering somewhat difficult the final clarification of the liquid.

When the neutralisation is complete the muddy liquor is run off into a reservoir, where it is allowed to remain ten or twelve hours to deposit the calcium sulphate. The clear liquid is filtered through granulated animal charcoal. The filtered sugar solution is then evaporated by steam heat until the hot liquid has a sp. gr. of 1·231, and when cold a sp. gr. of 1·296.

The syrup thus obtained stands a couple of days, during which the greater part of the calcium sulphate still remaining dissolved in the liquid separates. The clear liquid is then drawn off and sold in this state to brewers and confectioners. For finer kinds of confectionery and for liqueurs a syrup is required as free as possible from colour, and it is again passed through animal charcoal.

When hard sugar is required instead of syrup a little more acid is used in the saccharification, 55 or 60 lbs. being taken to every 2,000 lbs. of starch, and the liquid is evaporated till it has a specific gravity of 1·309 in the hot state, or 1·370 upon cooling. The syrup is then run into a large vessel and when it begins to crystallise it is run into tubs or moulds to solidify.

For the manufacture of sweetmeats, preserves, and fruit syrups, a glucose syrup is prepared containing some dextrin still unaltered. For this purpose only 14 or 15 lbs. of sulphuric acid are used for 2,000 lbs. of starch, and the syrup is evaporated until while hot it has a sp. gr. of 1·32, when it is passed boiling through a charcoal filter heated by a steam jacket.

The manufacture of the three products is essentially of the same nature, the only difference being that, in preparing the solid sugar, the saccharification of the starch is carried as far as possible, so as not to leave any dextrin unconverted, since the presence of that substance would hinder the crystallisation. The syrup used for liqueurs, etc. is required to be quite free from crystallisation, and at the same time it must have a high degree of concentration. On this account a considerable quantity of dextrin is left unconverted, and by this means there is obtained a dense viscid liquid that is readily soluble in water, but is not at all liable to crystallise. In ordinary starch sugar syrup the saccharification is almost complete, but the product is not concentrated to such a degree that it is capable of crystallising. The syrup used for liqueurs, and called by the French sirop impondérable, contains about 11 per cent. of water, and the dry substance it contains consists of 42 per cent. of sugar and 58 per cent. of dextrin. The starch sugar syrup of 1·296 sp. gr. contains 30 per cent.

of water, and in the dry substance it contains there is from 85 to 90 per cent. of sugar. The solid glucose contains from 10 to 12 per cent. of water, and the dry substance from 95 to 98 per cent. of sugar. The quantity of calcium sulphate in the solid sugar amounts to $\frac{1}{2}$ per cent. and in the liqueur syrup to $\frac{3}{10}$ per cent.

The manufacture of granular grape sugar was introduced by Fouchard in Neuilly. The saccharification is carried out in the way just described, care being taken to secure as perfect a conversion as possible of the starch, since large quantities of dextrin would retard the crystallisation. So soon as the saccharification is complete the liquid is neutralised, carefully filtered and evaporated in summer till it shows while hot a density of 1·262, and in winter in the same state a density of 1·242. The calcium sulphate is allowed to deposit in large clearing vessels situated in a cool place or cooled by means of serpentine tubes through which cold water is passed to prevent fermentation. After 24 or 30 hours the syrup is cold and clear; it is then brought to crystallisation in vertical tubs open above, furnished with a perforated bottom, the apertures of which are closed with little wooden plugs during the crystallisation. The tubs are placed upon a stand over a gutter lined with lead. After 10 or 12 days crystallisation commences. As soon as the liquid is charged to about two-thirds with crystals, the little plugs at the bottom of the tubs are drawn out and the syrup allowed to run out. The syrup is again boiled with sulphuric acid to convert the unchanged dextrin contained in it into sugar.

The drained crystals are placed upon gypsum plates in a drying oven and exposed to a current of air at a temperature of 22° or 25°. If the temperature were higher the crystals would melt in the adhering syrup and stick together. The formation of lumps is unavoidable even with the utmost care, and the dry sugar is therefore sifted and the pieces left on the sieve are broken between rollers.

Glucose or starch sugar, either in the solid form or in the state of syrup, is used for a variety of purposes: in brewing as a substitute for malt (see BEER); and in the manufacture of spirit. It is also used in the production of wine (see WINE). The dense syrup is chiefly used for preserving fruit, and in the preparation of liqueurs.

CANE SUGAR is chiefly prepared from the sugar cane and the sugar beet. Smaller quantities are prepared in Canada and the United States from the sugar maple (*Acer saccharinum*), in China from *Sorghum saccharatum*; and in India from the juice of the palm.

In North America, where the maple is indigenous and very abundant, the production of sugar from this source is a regular branch of industry. The process of manufacture is very crude: about the month of February or March, holes are bored in the trees to the depth of about half an inch into the white bark or splint of the stem, and the juice which slowly flows out is collected in troughs, from which it is transferred to the boiling pans, where it is rapidly evaporated, and skimmed meanwhile, until it is sufficiently concentrated to be filtered through woollen cloths. The syrup thus obtained is further boiled down and allowed to crystallise in moulds.

Culture of the Sugar Cane.—The sugar cane (*Saccharum officinarum*) is richer in sugar and contains less non-saccharine matter than any other sugar-bearing plant. When ripe it contains 90 per cent. of juice, having a saccharometer density of 15° to 20°, varying in the amount of sugar it contains from 12 to 22 per cent., but averaging about 18 per cent. The manufacture of sugar from the sugar cane has been known from the most ancient times. The methods of manufacture have in some colonies undergone many improvements in recent years; but in many places it is still so imperfectly carried on that a yield of 5 or 6 per cent. is with difficulty obtained.

The sugar cane comes from India and China. The inhabitants of those countries first used the juice of the plant as a sweet drink, and then prepared from it a syrup and crystallised sugar. The sugar cane flourishes only in countries with a tropical climate; in northern countries the product, and especially the amount of sugar, is much smaller. Different varieties are cultivated; the best of them are known as Otaheite and Batavia cane, and violet and striped violet canes from Java.

The cultivation of the sugar cane requires a generous rich soil, as free as possible from soluble salts and artificial manuring. A too large amount of salt in the soil, as it often occurs in the neighbourhood of the sea, is injurious to the quality of the cane, the salt passing into the juice and promoting the formation of molasses. In the absence of a sufficiency of stable manure, guano and fish refuse, and phosphates, flesh and blood manure, and bone black from Europe are used. During the last few years a considerable quantity of potash salts from Stassfurt, and of superphosphates, have been sent to the colonies. The manuring with blood in the colonies has given rise to a peculiar result; the rats allured by the smell seek out this manure, and eat not only it but the root stocks of the cane also, thus doing considerable damage. It is said that this can be avoided by mixing charcoal dust and soot with the blood.



Fig. 588.



Fig. 589.



Fig. 590.



Fig. 591.

The sugar cane can be raised from seed; this is done however only exceptionally, generally it is multiplied by cuttings. These cuttings are placed obliquely, at an angle of 45°, in small furrows 20 inches long, 10 inches wide, and 7½ inches deep, and covered with moist earth. Fig. 588 represents a slip which has already thrown up several rooting shoots. The first development of the young plant is shown in fig. 589. The slender stalk shoots upward, forming numerous knots, and throwing off first the lower and then the following leaves. Fig. 591 shows a plant two-thirds or three-fourths grown. The stalks are from 6 to 12 feet high, with a diameter at the centre of 1½ to 2 inches. The largest leaves are 3 to 4 feet long, and 1½ to 2½ inches broad. The leaves are longitudinally veined, and have very stout whitish nerves; the colour of the remainder of the leaf is green to yellowish green; the surface is smooth and the edges rough. After from twelve to fifteen months, according to the soil and the climate, the plant begins to flower; the upper part increases considerably in length (fig. 590), and there is formed a panicle of silvery white flowers.

Frequently it happens that the cane does not flower, and consequently it cannot then bear seed. The ripeness of the stalk is then recognised by its becoming yellow



Fig. 592.



Fig. 593.



Fig. 594.

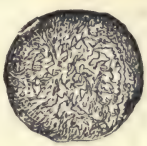


Fig. 595.

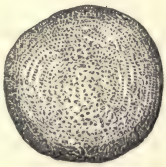


Fig. 596.

coloured, beginning from below. Figs. 592, 593, and 594 show sections of the cane in the ripe condition. The knots are separated from each other by a distance of 3 to 5 inches. The tissue at the knots is much harder and denser than that between them, and the sap there also is poorer in sugar; the further therefore the knots are from one another, and the longer the internodes, the more advantageous is the cane for working.

Fig. 593 shows the longitudinal section of a cane that has been split, in which appear a number of strong parallel fibres, packed closely upon each other near the exterior, but in the middle wider apart. Figs. 595 and 596 (on a larger scale) show these more clearly. They are the vascular bundles, formed of tubes and vessels imbedded in the parenchyma of the medulla, and are dispersed through the entire plant.

The sap contains various nitrogenous and non-nitrogenous substances, phosphates, alkaline salts, silica, and a very small quantity of an essential oil having an agreeable odour. Through this oil sugar prepared from the cane can be easily distinguished from beet sugar. The agreeable smell of sugar from the cane, as well as the molasses, allows of its immediate consumption; but an essential oil occurring in the beet imparts to beet sugar so disagreeable an odour that it cannot be eaten without previous refining.

Structure and Composition of Sugar Cane—A longitudinal section of the sugar cane in the ripe condition, when it has acquired a yellow colour and most of the leaves have fallen off, if examined proceeding from the exterior to the centre, presents the following points:—

1. A fine layer (*g g*, fig. 597), lying upon the cuticle, and consisting of a kind of wax, which Dumas examined and described as cerosin.

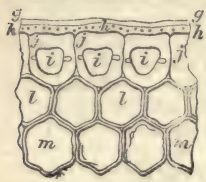


Fig. 597.

2. The cuticular layer (*h*) with square prominences, lying close upon the intercellular spaces of the tissue beneath.

3. Thick walls (*j j*, figs. 597 and 598) of long epidermis cells (*i i*). The separate cells lie close to one another, though a line of demarcation between them is perceptible. The cell cavities are in communication with each other through a delicate membrane by ducts in the cell walls.

4. A thin-walled cellular tissue (*m m*) under the epidermis (*l l*, fig. 597).

5. A somewhat thick-walled cell tissue, the membranes of which are traversed by pitted canals.

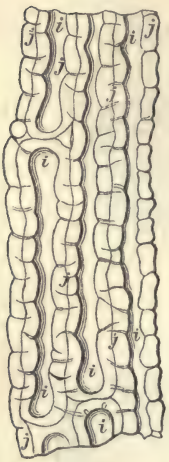


Fig. 598.

6. Two series of bundles of woody vessels, parallel with the surface, and surrounding a space filled with vessels. In the first series these vessels lie close to one another, in the second they are further apart. Similar bundles, but with fewer woody vessels, separated more widely from each other and lying in the midst of larger cells, occur as far as the centre of the axis of the cane.

The layers of cells between the epidermis and the first two series of woody bundles are free from sugar. The sugar is contained in the thin-walled cells which surround the vascular bundles in the middle of the stem.

In the ripe condition, all the tissues after washing with water are coloured yellow by iodine; an addition of sulphuric acid makes the colour more intense. The cuticle (*h*, fig. 597) is coloured orange. Upon treating the tissues with caustic soda, the albuminous substances situated in the cell membranes are dissolved and washed out. The membranes of the small pitted vessels and those of the sugar-bearing cells then give the cellulose reaction, being coloured blue when treated with iodine and sulphuric acid. The outer cell layers withstand the action of caustic soda; they become swollen and distorted, and are broken up into separate cellular portions, but they still continue to give the yellow colour when treated with iodine and sulphuric acid.

The younger the cane is, the more easily is the cellulose reaction produced. In young canes the sacchariferous cells, upon treatment with iodine and sulphuric acid, take at first a yellow colour; this is soon changed to green, and finally to blue. When a quite young shoot, 7 or 8 inches long, and still surrounded by the germinal leaves, is treated with aqueous solution of iodine the entire tissue, with the exception of the small pitted vessels, is coloured yellow. A drop of sulphuric acid produces in this a most beautiful microscopic appearance. The tissue of the knots, the cuticle, and all the inner parts of which are yellow, become violet through the entire thickness of their swollen walls; the cuticle and epidermis take a deep orange yellow colour, and the entire thickness of the cells of the underlying cellular tissue becomes blue. The small pitted vessels are also coloured blue, and form a blue cylindrical bundle, which is surrounded by a yellow portion, consisting of the large pitted vessels with their numerous pits, the circular vessels, and the woody vessels. In the middle of the latter can be seen the inner swollen layer, consisting of purer cellulose, which is coloured blue.



Fig. 599.

Throughout the young stalks and shoots occur also numerous spiral vessels (fig. 599); but these disappear afterwards, and are not detected in the ripe cane.

In the young stalks and newly formed leaves numerous starch granules occur; the stalks especially contain them in the tissue lying directly under the epidermis, and in the sugar-bearing cells surrounding the vascular bundles. They are also found in the cells surrounding the vascular bundles in the young leaves. In the ripe stalks these deposits of starch no longer occur, or at most in the upper and younger internodes. The richness of the sap in sugar is in proportion to the ripeness of the cane; in

the unripe condition it contains, besides starch, many other foreign bodies that exercise an injurious influence upon the crystallisation of the sugar. For this reason the tops and root shoots are removed at the harvest, and are used as cuttings for the next crop, as fodder, or as fuel. This occurrence of starch in the young parts of the plant, and its disappearance in the ripe parts, explains how it is that many analysts have found the juice of the sugar cane rich in starch, whilst others have not met with it.

The following table shows the composition of the sugar cane when ripe, and also in the first third of its development:—

Perfectly Ripe.

Water	71·04
Cane sugar	18·00
Cellulose, lignin, pectin, pectic acid	9·56
Albumin and three other nitrogenous bodies	0·55
Cerosin, chlorophyll, yellow, brown, and red colouring matters, fat, resin, essential oil, and an aromatic soluble substance	0·37
Insoluble salts 0·12; soluble salts 0·16; calcium and magnesium phosphates, alumina, calcium sulphate, oxalate, acetate, and malate, soda, potassium sulphate and chloride, and sodium chloride	0·28
Silica	0·20
	100·00

First Third of Development.

Water	79·70
Cane sugar and grape sugar	9·06
Cellulose and incrusting matters	7·03
Albumin and three other nitrogenous bodies	1·17
Starch, cerosin, chlorophyll, and yellow, brown and red colouring matters	1·09
Fat and aromatic bodies, hygroscopic substances, essential oil, soluble and insoluble salts, alumina, and silica	1·95
	100·00

According to Casaseca, the sugar is distributed in the Havanna cane in the following proportions:—

	Entire Cane	Peeled Cane	Rind
Water	77	77·8	69·5
Sugar, etc.	12	16·2	11·5
Ligneous substances	11	6	19

The amount of water in the sugar cane increases towards the top of the stalks, and the greatest amount of sugar is found in the lower third of the cane, much less in the upper third.

The average composition of the juice of the sugar cane is:

Water	81·00
Sugar	18·20
Organic substances precipitated by lead salts	·45
Saline substances	·35
	100·00

Although it may be assumed that in the ripe cane, only cane sugar, but no grape or fruit sugar, occurs, it may happen, through decomposition produced by mechanical injuries received during the gathering of the cane, that the juice to be manufactured will contain small quantities of both these kinds of sugar.

The quantity of cellulose, lignin, etc., is dependent upon the greater or less distance between the knots, as the tissues of the nodes are much more dense than those of the internodes. The pectic acid is also combined with bases.

The aromatic soluble substance is soluble in cold 95 per cent. alcohol; it is precipitated by tannin, and at the temperature of boiling is coloured red brown. According to Plagne and Hervy, this substance has the property of converting the sugar into a viscous, tasteless substance, and of preventing the alcoholic fermentation. It can be removed by filtration of the cold juice through animal charcoal.

According to Payen's observations cane juice contains acid calcium and magnesium

phosphate. The addition of a slight excess of ammonia produces a crystalline precipitate of ammonio-magnesian phosphate (0·09 per cent.), besides a flocculent precipitate, which, collected and treated with sulphuric acid, yields calcium sulphate and acid phosphate. Under the influence of air and ammonia the juice is coloured brown.

From the foregoing figures it appears that the unripe cane contains only about half as much sugar as the ripe cane and about a third less tissue-forming material; on the other hand, it contains three times as much foreign or non-saccharine substances. These differences make it evident that in districts where, through climatic influences, the cane does not come to perfect maturity, either a very insufficient yield of sugar is obtained or only syrup can be produced; whilst in hot countries where the plant attains its normal maturity, it yields a cane containing but little non-saccharine material.

The knots of the cane are formed of a dense tissue, in which woody vessels with thick walls predominate. The membranes of all the cells are here much thicker than in other parts; and the sugar-bearing cells are smaller and less numerous. The proportion of sugar is consequently hardly half as high as in the internodes. As the cells not filled with sugar contain other constituents, the sap in the nodes is proportionally inferior.

The ripe canes are cut down close to the base, and carried to a warehouse near the boiling house. The flowering stalk and the leaves are removed; and the four or five upper knots, containing less sugar, are cut off, and used as cuttings, fodder, or fuel. Further, all the canes that have sustained mechanical injury—those broken by the wind or gnawed by the rats—must be carefully separated, as these readily commence to putrefy, and the fermentation may spread through the whole contents of the warehouse. The juice from these injured stalks is mixed with molasses, and used in the manufacture of rum.

The harvest of canes varies very much in the different colonies according to climate. The following quantities are said to represent the average yield per acre for the fifteen months period of growth: Martinique, 20 cwts.; Guadeloupe, 24 cwts.; Reunion, 40 cwts.; Brazil, 60 cwts.

Culture of the Sugar Beet.—Although the manufacture of beet sugar dates back but a few decades, its development during this period has progressed more rapidly than that of the old methods of preparing sugar from the sugar cane.

It is now one of the most important of agricultural industries. It can be carried on profitably and well only when the producer of the raw material—the beet root—is at the same time interested in its manufacture into sugar. When this is not the case, there is a possibility that the producer of the raw material, looking after his own interests only, will endeavour to raise as many roots as possible upon his land irrespective of their quality. But the cultivator who is at the same time a sugar manufacturer directs his attention to raising sugar-producing beet roots, in order that he may bring to the factory a superior raw material.

Properly carried on, the cultivation of the sugar beet is greatly beneficial to other agriculture. The deep and careful cultivation which the beet requires greatly improves the land, the soil becoming thereby considerably deepened, and the disintegration and solution of the mineral constituents greatly accelerated.

The tap-root of the beet, which is 3 to 6 feet in length, descends to a great depth, loosening the subsoil, and drawing the greater part of its nourishment from a depth of soil which most other plants fail to reach. The nourishment thus obtained passes partly into the leaves, and is left with them upon the ground, after the gathering in of the crop. When the sugar manufacture is carried on in connection with the beet cultivation, all the constituents of the beet, with the exception of the carbon obtained from the atmosphere, can be returned to the land, since the refuse of the factory—the heads of the beets, pressings, lixiviated residue, molasses, etc.—is consumed by farm stock and becomes converted into manure, while the residuary products and the bone black used, etc.—are, either immediately or after preparation, incorporated with the soil. By such a method, in which only raw sugar, an organic substance almost free from nitrogen or ash, is withdrawn from the soil, it is not exhausted.

In very few sugar factories, however, is the molasses used for fodder, but it is sold, and with it many important constituents of the soil—potash salts in particular. Nevertheless, commercial manures are quite capable of supplying the deficiency occasioned by the sale of molasses.

On the other hand, the culture of the beet, improperly carried on, with no provision made to return to the land the constituents taken away, is most exhausting. The consequences are, that the beet roots first deteriorate in quality, producing a less amount of sugar, then fall off in quantity, and at last become stunted and liable to disease. Roots that appear sound when gathered, become in a short time decayed and afterwards completely rotten.

Further, when beets are raised too often upon the same ground, the crops suffer much from various parasites, animal as well as vegetable, which increase in the beet fields, in the most surprising manner. Among the enemies of the beets, the cockchafer or May bug is especially prominent, the larvæ remaining for a number of years in the ground and making great havoc among the young plants.

The mole cricket or fen cricket (*Gryllotalpa vulgaris*, Latr.) is another insect which has lately shown itself exceedingly destructive to the beet, as it feeds upon the roots of the beets which stand about its nest. Another enemy is the beet worm. Of vegetable parasites there are the beet killer (*Rhizoctonia violacea*, Tul.), a fungus which appears in reddish-brown spots upon the surface of the roots, and passing inwards, causes rottenness and complete destruction of the beet, and the beet blight (*Uromyces betæ*, Tul.) which attacks the leaves.

For the cultivation of the beet, a dry, or at least well-drained, generous deep clay soil, containing some lime, should be selected. This should be broken up, as soon as the preceding crop has been got in, in order to destroy the weeds; after a little time it should be ploughed as deeply as possible, and then left lying during the winter in great furrows. As a thorough preparation of the soil is essential to the success of the beet culture, in many sugar-producing districts the steam plough is profitably employed, no other implement being able to do the work so regularly and thoroughly. Except levelling and a slight loosening of the heavy soils, or compacting the lighter ones by means of rolling, little should be left to be done in the spring, as disturbance of the soil at this season is disadvantageous to the proper growth of the beet.

Fresh stable manure should never be used for beets, although it may be profitably used for the preceding crop. Liquid manures are valuable, but should only be employed in autumn. In beet culture extensive use is made of commercial manures, such as guano, superphosphate, and potash salts. The use of the latter should never be neglected, unless the soil itself be especially rich in potash, as it is potash in particular which is needed by the beets, and it is also removed in great quantities in the molasses. In using the potassium salts from the Stassfurt factories, they should be brought upon the ground in autumn, and carefully distributed in the soil. By this means, the foreign salts contained in this fertiliser become dissolved by moisture, and partly washed away, while the potash in contact with the soil becomes absorbed and retained in an insoluble form. Guano and superphosphate are spread upon the ground immediately before planting, and are incorporated with the soil by means of the harrow. These fertilisers may be most profitably used incorporated with one another, in the proportion of one part of guano to two or three of superphosphate. It often happens that manuring with guano alone, or the use of large quantities of it, so greatly accelerates the growth of the beets, that they pass through the whole course of their development the first year, and shoot up into seed, instead of producing roots containing sugar. This is avoided by using a moderate amount of guano mixed with superphosphate.

The work of planting should be done as early as possible, so as to afford the plants a long growing season, and yet enable the factory operations to be begun early in autumn. It is necessary to wait until the close of the spring, as the land should no longer be wet, but thoroughly warmed by the sun, so that the young plants may soon spring up. For the early growth, warm weather and a moderate amount of rain are most favourable.

The interval between the plants should not be too great, or else, though the growth goes on rapidly, and the crop is large, there is little sugar yielded. Other circumstances being equal, the roots are rich in sugar in proportion as they remain of small size, and stand near together. Yet as this implies a considerable diminution in the crop, the question is to get a satisfactory quantity of roots, and yet such as are rich in sugar. The extreme distance between individual plants found advisable is 1¼ feet each way; but the interval is frequently less. Roots are thus obtained of medium size, averaging in weight from 1¼ lbs. to 1¾ lbs.

The plants usually reach maturity some time in September, according to the time of sowing, and the condition of the weather during the period of growth. The root no longer increases in volume, and the leaves begin to wither, commencing at the outer circle. Warm rains followed by warm weather at this period are especially damaging, causing the beet to begin a new growth, and to send out new leaves from the middle of the plant. The ingredients of the sap stored in the root are used in the formation of these new leaves, and the consequence is a root containing but little sugar. The most favourable beet crop is obtained when the withering of the leaves is accompanied by rather dry and cool weather.

The roots are gathered one by one, being raised out of the ground by means of a spade; the leaves are removed, and the roots are buried in pits until required for use in the factory. To remove the leaves the usual custom is to cut off the upper part

of the beet with the leaves attached, but sometimes they are wrenched off with the hand, leaving the root entire, by which method the inner part of the root is less exposed to the action of the air and remains sounder. The leaves should never be removed before the beets are gathered. The pits used for storing the roots are usually dug in the field itself as near as possible to the road, so as to admit of the beets being easily carted away. The pits are prepared in a way similar to those used for storing potatoes (see p. 787). Some manufacturers prefer large pits, others again select pits of smaller dimensions; some cover in their pits deeply at once, others prefer to wait until cold weather sets in; in every case the chief object in view is to keep the pits dry and preserve them against a change of temperature. The pits should be well protected against the winter frosts, and against a sudden occurrence of warm weather in the spring. The frosts of winter are hardly more damaging than warm weather in the spring, which causes the beets to sprout in the pit, and lose a considerable part of their sugar. Loss of sugar goes on during the whole of the time the beets are kept, so that even the best contain considerably less sugar in February than in October, and in March and April the loss increases. The storing time should therefore be reduced as far as possible by working up the beets quickly.

The choice of seed has great influence upon the quality of the beet crop. There are many varieties of beet, all of which have proceeded from the white sugar beet originally cultivated in Silesia. Where plants of good quality are at hand, it is well to raise the seed from them, provided the field where they are grown is sufficiently distant from other fields of seed beet; if this precaution be not taken, it is impossible to guard against hybridising. To the proper culture of the beet seed, the German manufacturers are greatly indebted for the high position which the sugar industry has reached among them, they being in this respect far beyond their French competitors. Generally it may be stated that in the German factories 9 per cent. of crystallised sugar is obtained from the roots, while the French do not get more than 6 to 7 per cent.

Anatomical Structure of the Sugar Beet.—If a sugar beet be cut, its cross-section exhibits a number of concentric rings. At the exterior are seen five or six courses of cells which form the epidermis. These cells consist of much thickened membranes, and contain albumin, oil, salts of calcium and silicic acid. Frequently the epidermis is bruised or injured during growth, and when this occurs the underlying cells become converted into epidermis by thickening of their membranes, thus making compensation for the injury, and securing the protection of the tissues underneath. This, however, is not a peculiarity of the epidermis of the sugar beet, for the same phenomenon is observed in all plants provided with an epidermis.



FIG. 600.

Immediately under the epidermis lies a layer of cells rich in protoplasm, which, when the plants are exposed to the light, form chlorophyll; to this is due the green colour of that part of the beet which is not covered by the earth. The whole of the remainder of the beet consists of parenchyma, in which vascular bundles are symmetrically disposed in concentric circles. The parenchyma consists of small cylindrical roundish or polyhedral cells, and is recognisable in the beet by its white colour and its structure. The circularly disposed vascular bundles may be seen with the naked eye, and are easily distinguished from the parenchyma. The parenchyma cells are filled with the sugar sap, and in good beets this kind of tissue is present in considerably greater quantity than in beets of inferior quality—a fact which allows the value of different kinds of beets to be approximately estimated.

The anatomical structure of the sugar beet is shown in fig. 600 which represents a longitudinal section of the sugar beet, showing the spindle shape, and the long tap root reaching from 3 to 6 feet. In digging, the root is usually torn off at the point N, and remains in the ground, producing by its decomposition and decay a mellow condition of the soil, its constituent elements becoming available for future crops.

The head of the beet (*b c*), which protrudes from the ground, assumes a green colour upon exposure to the light; it contains little sugar, but more foreign matter than the remainder of the beet. Hence those varieties are preferred of which the largest portion possible grows under the earth. The disadvantage would be very great if the part above ground extended as far as is shown by the letters (*a d*). Upon the top of the beet (E) is a pithy spot containing much water and salts, and but little sugar. The tissue which forms this pith easily undergoes change during the ripening of the plant, cavities being produced through degeneration of the cells. At a later period this decomposition readily extends to the other parts of the beet.

The white zones (A B C D E) in this section show the sugar-bearing tissues which surround the vascular bundles. The part of the beet between these rings either contains very little sugar or none at all.



FIG. 601.

Fig. 601 shows a cross-section of the same variety of beet, in which the position of the concentric layers is very noticeable. In the middle, round the axis of the root, may be seen the vascular bundles surrounded by the sugar-bearing tissues, which gives to this part the appearance of a ringed surface (A). Another circle (B) similarly shows the vascular bundles surrounded by sugar-bearing tissues in this region. The remaining concentric circles (C D E F) correspond to the same parts.

Fig. 602 is a representation of a cross-section as it appears under the microscope and shows the details more clearly. The zones of vascular bundles are shown at (A B C D) with the sap-bearing vessels (*a a a*) in the midst of these zones, and beneath

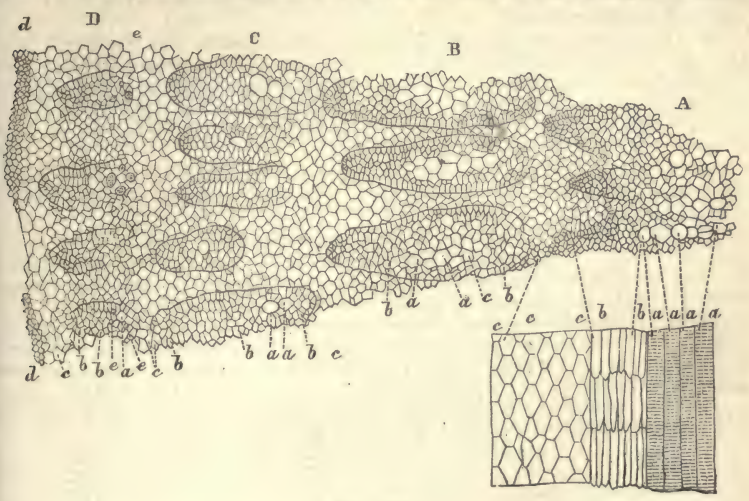


FIG. 602.

is a longitudinal section of such a zone, the sap-bearing vessels being here also shown at *a*. The letter *b* in both sections marks the cambium portion of the vascular bundles, the cells of which are considerably elongated. The parenchyma lying between the vascular bundles, which contains the sugar, is shown at *c*. The parenchyma cells become more approximated to each other towards the surface of the beet. In the outside ring are dark semi-transparent cells (*e e*) around an isolated vessel, the dark cells being again surrounded by sugar-bearing cells. The dark cells (*e e*) contain small crystals of crystalline agglomerate of calcium oxalate, and they are found in the greatest quantity near the head of the beet.

Fig. 602 shows also the epidermis tissue (*d d*), consisting of four or five layers of cells, the membranes of which are impregnated with silicic acid, calcium salts, and fatty and nitrogenous substances. Under the epidermis is a layer of cells rich in protoplasm, and in the red varieties, containing the red colouring matter which forms

chlorophyll upon exposure to light. At *d'* is shown a lesion of the epidermis, where the cell layers lying under it have become changed into epidermis.

Composition of the Beet.—By far the greater part of the sugar beet consists of water and substances dissolved in water. If the beet be reduced by attrition upon a rasp, or pulper, so that the cellular membranes are thoroughly broken up, a pulp is obtained from which, by treatment with water, all that is soluble may be removed, leaving the cell membranes and the insoluble constituents of the tissue. When dried this residuum is equal, upon an average, to 4 per cent. of the weight of the beet. The variation in the amount of residuum is never very great, being never below 3 or exceeding 5 per cent. It can therefore be assumed that the beet consists of: pith or residue 4 per cent., sap 96 per cent.

The composition of the sap is influenced greatly by the quality of the beet, the nature of the soil, the manuring, and the character of the weather. Even if beets be grown throughout under similar conditions, they will exhibit the greatest diversity of composition in individual specimens. In an examination of about one hundred specimens of beets grown under like conditions upon the same field, it was found that the dry substance varied between 13·37 and 21·52 per cent., the mean of all the observations being 18·19. If the amount of insoluble residue be estimated at 4 per cent., the following will be the result:—

	Maximum	Minimum	Mean
Sap ingredients	17·52	9·37	14·19
Water.	78·48	86·63	81·81
Insoluble residue	4·00	4·00	4·00

By far the largest part of the sap ingredients is sugar (cane sugar), but the proportion varies within wide limits, dependent upon a variety of circumstances.

1. *The quality of the Seed.*—There are so-called sugar beets, the proportion of sugar in which, under even the most favourable circumstances, does not amount to more than 8 or 9 per cent., while other choice seeds produce beets containing 17 per cent. and upwards of sugar.

2. *The nature of the Soil.*—A soil unsuited to beet culture, even if the seed be of the best, will not yield beets containing so much sugar as is secured from beet grown in more suitable soil. If a great amount of stable manure is used also, the crop of beets will be large, but will leave much to be desired as to quality. Repeated experiments have shown that beets manured in autumn with potassium salts are much richer in sugar than those not thus manured.

3. *The size of the Beets.*—Usually the larger the beet, the poorer it is in sugar; the greater the circumference, the greater the amount of water and foreign elements contained in the sap.

4. *The Weather.*—The weather has the greatest influence upon the beet at the close of its growth, when the plant is maturing. If, in consequence of rain followed by warm weather, the ripe beets commence a second growth, the quantity of sugar diminishes daily, it being used up for the nourishment of the new leaves.

5. Other causes which cannot be explained co-operate with those mentioned, and the result is that beets grown under similar conditions, raised from the same seed, upon the same ground, and in the same year, are never found to contain precisely the same percentage of sugar and other constituents.

Experiments made upon about one hundred specimens of sugar beets gave the following percentage composition of the juice:—

	Maximum	Minimum	Mean
Sugar	17·68	9·56	13·93
Other substances	3·51	·38	1·73
Water	81·20	87·65	84·45

There being so great a diversity as to the quantity of sugar in individual specimens, it is plain that no correct estimate can be formed of the amount of sugar contained in a large quantity of beets, even if they have been grown in the same field. It is important to bear in mind the great liability to error, in drawing conclusions from the results of single experiments as to the amount of profit to be derived from the manufacture of considerable quantities. In order to get tolerably correct data for determining the amount of sugar in quantities of beets, the juice from twenty, thirty, or even fifty specimens should be well mixed and then examined. Of the remaining ingredients of the juice, the following may be mentioned:—

Grape Sugar and Fruit Sugar.—In beets of good quality, mere traces or none at all of those kinds of sugar are found; they result from the transformation of cane sugar through the rotting or germination of the beet. Their presence is disadvantageous, owing to the fact that, in the process of refining the juice, they remain in the

alkaline solution, and quickly decompose upon contact with the air, imparting a dark colour to the juice, that requires a considerable expenditure of bone black for its removal.

Organic Acids.—Oxalic, tartaric, citric, malic, and some other acids, combined with potassium, sodium, calcium, magnesium, and other bases, sometimes as neutral, and sometimes as acid salts. In the refining of the juice the acid salts are neutralised by the addition of lime, and the acids previously combined with alkalies become for the most part converted into calcium salts. The calcium salts occurring in the sap of the beets combined with organic acids are usually insoluble in water; they are therefore removed in the process of clarifying. But their removal by this process is not complete, owing to the fact that the salts insoluble in pure water are slightly soluble in water containing sugar in solution. Consequently a portion of the calcium salts remains in the juice, and is afterwards removed by means of animal charcoal.

Gum, Starch, and Fatty Substances.—These substances occur only in very small quantities, and are easily removed in the first process of clarifying, and by the treatment with animal charcoal.

Colouring Matter.—In the undamaged beet the juice is colourless, but as soon as it comes into contact with air, it becomes coloured, first, of an indefinite grey colour, then reddish, and frequently a rather deep brownish red; after long exposure to the air it becomes almost black. The composition and properties of this colouring matter which thus decomposes upon exposure to the air are not known. It is easily removed from the juice by treatment with lime or basic lead acetate. The red varieties of beet contain also a red colouring matter in the sap. The part of the otherwise colourless beet which grows above the ground always contains chlorophyll in the outer cell layers.

Albumenoids.—Among the different albumenoid compounds in the beet is albumin itself. Upon heating the sap, this curdles into flakes insoluble in water and separates out as a scum. Upon treatment with alkalies the albumin, which is otherwise insoluble in the boiling liquid, becomes decomposed and goes partly into solution. The removal of this dissolved albumin is extremely difficult, a part of it always remaining in the juice and in a modified form in the syrup. Albumin being itself incapable of crystallising, prevents the crystallisation of sugar also. The smaller, therefore, the proportion of albumin contained in a beet juice, the better it is fitted for the operations of the factory, and methods of obtaining the juice must be estimated according to the relative amount of albumin in the juice they yield.

Asparagin.—A nitrogenous organic substance, widely distributed in the vegetable kingdom, which may be considered as an amide of malic acid. Upon boiling with alkaline fluids in the clarifying process, asparagin is decomposed into aspartic acid and ammonia, the latter escaping with the steam.

Betaine.—A nitrogenous organic base discovered by Scheibler in beet juice, the composition of which is represented by the formula $C_{15}H_{33}N_3O_6$. It is very soluble in water, and is not removed from the juice during the manufacture, but passes into the molasses in the crystallising process.

Ammonia and Nitric Acid.—The first is combined with different acids, the latter chiefly with potassium. The ammonium salts are decomposed in the clarifying process, the ammonia escaping during the boiling of the juice, giving rise, together with that from the decomposition of asparagin and albumenoids, to the penetrating smell of ammonia which is present in a sugar factory, especially in the neighbourhood of the clarifying vessels. The amount of ammonia escaping is sufficiently considerable to render its recovery desirable. According to some experiments of Reiset, juice from different kinds of beets yielded 0·441 to 0·775, or on an average 0·634 parts per 1,000 of ammonia. In a daily consumption of 50 tons of beets, this would represent about 66 lbs. of ammonia, or for the whole season of five months about 4½ tons, which would represent a large sum could it be utilised in manure. The proportion of nitrates varies from the merest traces to considerable quantities, the amount being dependent upon the richness in these compounds of the soil in which the beets are grown. Potassium nitrate being very soluble in water, it is not removed during the manufacture, but crystallises out with the sugar. Raw sugars have come into the market, especially from Russia, which have contained a very large proportion of potassium nitrate.

Other Inorganic Substances.—Potash, soda, lime, magnesia, ferric oxide, phosphoric acid, sulphuric acid, and chlorine, are never-failing constituents of plants, and are therefore always found in beet juice. They are partially removed during the manufacture, and part passes into the sugar, but the largest proportion is found in

the molasses. Many other substances occur in the beet juice, concerning the nature and properties of which nothing is yet known. They are the substances called extractives, which require to be further studied.

The constituents of the juice, other than cane sugar and water, are all included under the name of non-saccharine matters. The relative behaviour of the individual members of this group varies greatly; some may be very easily removed from the juice, others require a considerable expenditure of clarifying material; others again cannot be got rid of at all, while some so greatly hinder the crystallisation that a portion of the sugar is consequently lost. Hence, the value of a beet for sugar manufacturing is not dependent alone upon the amount of sugar it contains, but the amount of non-saccharine matter is also very important. Two varieties of beet containing the same *quantity* of sugar may yield widely varying amounts of crystallised sugar. For example, a beet which contains 14 per cent. of sugar and 2 per cent. of non-saccharine matter will give very satisfactory results, while another also containing 14 per cent. of sugar, but with 4 per cent. of non-saccharine matter, will hardly pay for working up.

In estimating the value of a specimen of beet, therefore, the relative proportions of sugar and non-saccharine matter should be accurately determined. As every constituent which is neither sugar nor water is non-saccharine, it is sufficient to determine the amount of dry substance and of sugar in the juice. The amount of sugar is determined either by an hydrometer or by polarisation (see p.)—the dry substance by evaporating a previously weighed or measured quantity of the juice, and weighing the residuum. The difference between the percentage of dry substance and of sugar gives the amount of non-saccharine matter. The determination of the dry substance in the juice is not easy, some aptitude in chemical manipulation, and the expenditure of considerable time while the evaporation is going on, being necessary. Results sufficiently accurate for most purposes may be obtained by means of the saccharometer. The saccharometer made by Brix and others is a hydrometer, the tube of which is graduated in such a manner that each division represents 1 per cent. by weight of sugar, in a liquid containing sugar in solution. If, for instance, the instrument sinks in a solution of sugar to the 15° of its scale, the solution contains 15 parts of sugar in every 100 parts of the mixture. If the solution contains, besides sugar, another substance having precisely the same specific gravity, the reading of the saccharometer gives the percentage weight of sugar and the foreign substance together. If, however, the specific gravity of the substance in solution with the sugar differs from that of sugar, the saccharometer no longer gives the precise amount of dry residue. For example, in a solution containing 14 per cent. of sugar and 2 per cent. of some substance having a specific gravity higher than that of sugar, the saccharometer will register more than 16°. If, however, the specific gravity of the second body be less than that of sugar, the saccharometer will indicate an insufficient proportion of dry residue.

As, however, sugar forms in all cases the principal constituent of beet juice, whilst non-saccharine substances occur in relatively small quantities, and as moreover these non-saccharine matters consist of a mixture of substances of different specific gravities, many being of the same specific gravity as the sugar, some greater and some less—the saccharometer always gives results which are sufficiently exact for most purposes. In practice, therefore, it is generally used for determining the amount of dry residue, the difference between the results of the saccharometer and the polariser being taken as indicating non-saccharine matter.

For example, the saccharometer shows 16° or 16 per cent., and by polarisation 14 per cent. of sugar is found; the juice then contains $16-14=2$ per cent. of non-saccharine matter, or $\frac{14}{16}=0{\cdot}875$ of sugar. This fraction, which thus shows the proportion both of dry residue and sugar, is called the sugar quotient or sugar factor, and indicates that in 100 parts of dry substance in the juice examined, 87·5 parts are sugar, and 12·5 are non-saccharine.

Similarly a non-saccharine factor can be obtained showing the relation of sugar to non-saccharine matter. In the example given, the fraction is $\frac{2}{14}=0{\cdot}143$, the non-sugar quotient, which indicates that, for every 100 parts of sugar in the juice, there are 14·3 of non-saccharine constituents.

Besides the constituents of the juice, those of the pith have also to be considered. When the pith is completely deprived of sap, it consists essentially of the membranes of the parenchyma cells, and of the more or less woody portions of the vascular bundles, the whole cemented together by pectous substances. Neither the pure cellulose nor that which is partly converted into wood is of significance in the sugar manufacture; for should some of it pass into the juice, it simply causes a mechanical turbidity which is very easily removed. With the pectous substances it is however entirely different. They become converted into metapectic acid, upon being subjected to the

action of alkaline liquids. This acid, combining with the lime during the clarification, becomes converted into non-crystallisable calcium metapectate. Since all non-crystallisable bodies impede the crystallisation of the sugar, the presence of this calcium metapectate is a hindrance to the proper working up the juice. For this reason the mixture of any pith with the juice should be carefully avoided.

The Operations of the Sugar Factory.—The production of sugar consists essentially of a number of operations, partly mechanical, and partly of a chemical nature, carried on in various ways, and by the aid of apparatus of various construction. They consist in—

1. The extraction of the saccharine juice.
2. The treatment of the juice with the object of separating dissolved and suspended impurities.
3. The evaporation of the clear juice.
4. The crystallisation of the sugar.

According as the material from which sugar is to be obtained is sugar cane or beet root, the several operations carried out differ somewhat in detail, though they are essentially of the same nature.

Expression and Preparation of the Juice.—The working of sugar cane is carried out in various ways. Many factories have still the simplest and most imperfect arrangements; others are provided with all the improved apparatus used for similar purposes in the beet-sugar manufactories.

In the older factories, the juice is obtained by simply crushing the cane between channelled stone cylinders; in many factories iron cylinders are used. The motive power is variously water, wind, horses, or cattle, and sometimes steam.

The juice runs from the cylinders through a trough into a collecting vessel, where it stands for an hour to allow fragments of crushed cane, sand, etc., to deposit. This delay before the defecation is however highly injurious, as it may allow of the commencement of fermentation.

An essential improvement has been obtained in the colonial manufactories by the introduction of more perfect presses. Whilst the old presses scarcely squeezed out half the juice, the newer presses at first gave 60 to 65, and afterwards by further improvement 70 to 72 parts of juice from 100 parts of cane.

These presses consist of three hollow cast-iron cylinders, mounted horizontally in a strong iron frame. By means of pressure screws, which move the bearings in which the individual cylinders revolve, they may be brought nearer to or removed further from each other. One of the cylinders is set in motion by spur wheel and pinion, and toothed wheels on the axes of the other cylinders work in one another so as to communicate the motion to them. The cane to be pressed is carried upon an endless band to an inclined staging, and passed between the first pair of cylinders, where it is pressed flat, and is then pressed a second time between other cylinders. As the interval between the first pair of cylinders differs from that between the second pair, the pressure on the cane varies. At first it is only crushed.

In order to allow the juice time to flow away, the motion of the cylinders has to be a very slow one. From 70 to 75 parts of juice are obtained in Cuba and Réunion from 100 parts of cane.

This satisfactory result is due to the great solidity of the presses and their mountings, and also to the slow motion given to the cylinders, which make only one revolution in two minutes. In order to increase the production, this slowness of motion is compensated by large dimensions, the cylinders constructed having sometimes a diameter of $3\frac{1}{4}$ feet, and a length of nearly 7 feet. They yield daily from 70,000 to 90,000 gallons of juice, and are driven by 90 horse power.

The more perfect removal of the juice causes however a scarcity of fuel. When only half of the juice is pressed from the cane, the trash from 100 parts of cane still contains 10 parts of fibre and 10 parts of sugar, corresponding in heating value to 20 parts of wood. When 70 parts of juice are obtained, there remains in the trash only 4 parts of sugar together with 10 parts of fibre, representing only 14 parts of combustible material analogous to wood, or nearly one third less than before. But with this smaller quantity of fuel, there is two fifths more juice to evaporate. The improvement in the presses therefore necessitates an improvement in the evaporating apparatus.

It often happens that several knots in the cane come simultaneously between the cylinders, or that a foreign body may enter, and cause so great a resistance, as to endanger breaking a necessary part of the apparatus. In order to prevent this, one of the least important, because easily replaced, parts of the machine, the shaft which communicates the movement to the pinion of the larger wheel, is made comparatively weaker. If therefore a stoppage takes place, the probability is that this shaft will give way. A reserve of shafts is therefore provided, so that the broken one can be replaced, and the working proceed without loss of time. Another more suitable

method consists in connecting one of the wheels with the principal shaft by a friction coupling; if the resistance should then be too great, the wheel remains stationary, the shaft overcoming the friction of the coupling.

The yield of juice may be still further improved by heating the cylinder of the press with steam. The heat causes the cane to lose part of its elasticity, and allow the juice to flow out more freely, whilst the cane also expands less upon the removal of the pressure, and therefore sucks up less juice.

In the manufacture of sugar from beet roots the extraction of the juice requires to be preceded by a cleansing operation by which they are first freed from earth, sand, stones, grit, etc, so as to avoid injury to the machinery in which they are afterwards worked up. For this purpose a washing cylinder is used, such as is described on p. 764. It consists essentially of a long cylindrical body, made either of wooden laths, or of perforated iron surrounding a revolving axis, which with its barrel is supported in a large trough corresponding in size and filled with water. At one end of the cylinder is an opening for the introduction of the beets, and at the other is a self-acting arrangement by means of which the beets are removed from the wash. By means of suitable cog-wheels, the cylinder is rotated ten or fifteen times per minute; the beets are thus set in rapid motion in the water, so that the earth clinging to them is loosened and rubbed away. Sand and stones at once sink, and fall through the openings of the cylinder to the bottom of the vat, from which they are from time to time removed. The lighter portion of earth remains incorporated with the water, and is removed either by renewing the water from time to time, or by a constant stream of water running through the vat. By slightly raising the temperature of the water, the removal of tough clay is greatly facilitated. This is effected by means of a steam pipe laid along the floor of the vat; but it is only necessary when the beets are very clayey or have been frozen while buried. In the last case the frozen earth should at once be thawed away in warm water.

The more carefully the washing is performed, the less will be the damage to the machinery in the subsequent operations. But a thorough washing can only be effected by allowing the beets to remain a long time in the cylinder. It cannot be done by violent action, which has the further disadvantage that it injures the beets, destroying the small roots that contain relatively most sugar.

Different modes of carriage are used to carry the beets from the place of storage to the washing cylinder. One arrangement is shown in fig. 603; figs. 604 to 606 represent parts of the washing cylinder.

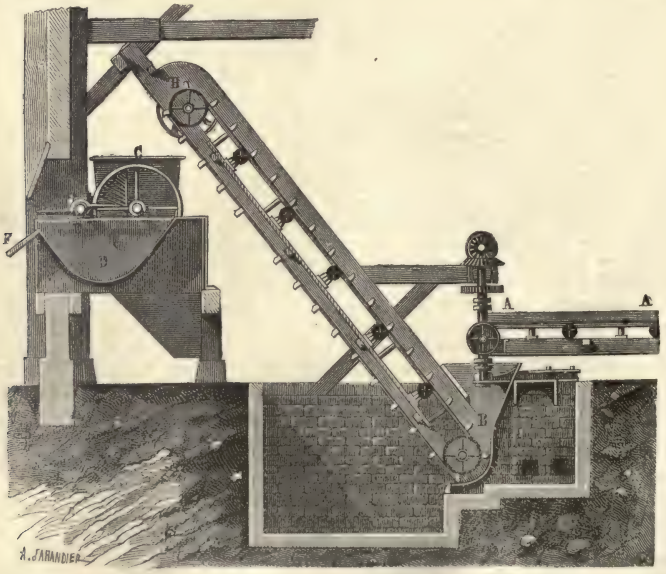


Fig. 603.

The beets are thrown upon an endless band (A, fig. 603) formed of iron rods united to each other by means of joints. This band, supported by rollers, revolves round

cylinders, and the beets are thus carried forward to the chain-pump work (B), by which they are raised, and allowed to drop into the hopper (C) of the washing cylinder. The construction of this cylinder as well as the chain arrangement is shown in figs. 604, 605 and 606, where the washing cylinder is united with a rinsing apparatus. By means of the trap arrangement, the beets are thrown into a second vessel (D), contain-

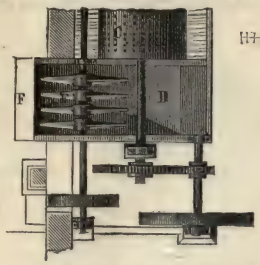


FIG. 604.

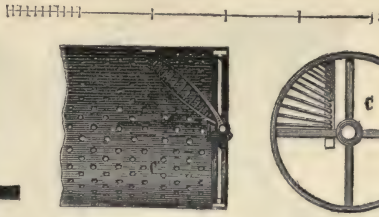


FIG. 605.

FIG. 606.

ing water in which is a stirrer with screw-shaped arms (E). The beets being freed from all coarse dirt, are placed in the rinsing apparatus, which contains clean water, and are there cleansed from any dirt that may remain. They are then thrown upon the sloping surface (F), and are carried away for further operations.

If possible, it is well to have the washing apparatus in a low situation, such as in the cellars of the factory; but of course this is only practicable where the nature of the ground will allow the dirty water to flow away. The beets may then be brought immediately from their place of storage to the wash-hopper upon the inclined plane, the washed beets being afterwards raised to the ground level by means of a chain-pump or other arrangement.

The next operation is to remove by means of a knife the fine rootlets growing from the side of the beet, also the green coloured upper part of the beet called the beet head, which grew above the ground, and lastly the rotten specks. In this process every single beet is subjected to a close inspection. To expedite this work, various kinds of machinery have been constructed. For removing the beet tops a knife is used, one end of which is fastened to a block by means of a hinge, while the rotten portions are removed by a rotating bent blade ending in a point. Some manufacturers, however, altogether dispense with this machinery, for although time may be gained by it, the work is never so well done as by hand. There is, however, a very useful arrangement called the beet round-about used for bringing the beets in the best manner to the workmen who are to trim them. It consists of a perforated iron plate surrounded by a rim, and revolving in a horizontal direction. The beets upon coming from the wash, fall upon the conical case surrounding the vertical shaft, and slide toward the rim of the plate. The labourers are posted around, and are able to seize the beets in the most convenient position for trimming. Frequently another washing takes place upon the round-about, a fine spray of water being brought to play upon the beets by means of a strainer-like arrangement; the dirt is carried off through the perforations in the plate.

In Germany, the trimmed roots are next thrown into a box-shaped, sheet-iron weighing machine, having a perforated bottom, and again rinsed; when the water has drained off, they are weighed by the customs officer.

The reduction of the beets is effected either by grating them to a fine pulp or cutting them into thin slices, according to the method by which it is intended to obtain the juice. As the juice is contained in closed cells, which while closed either yield no juice at all, or only yield it under strong pressure, it is requisite to burst these cells by rupturing the membranes. This tearing is done by means of graters which correspond essentially in their construction to those used in the manufacture of starch (*vide* STARCH).

The beet grater was invented by Thierry, and consisted originally of a cylinder, the frame of which was formed of saw blades placed at a little distance from each other. This cylinder is still used almost unaltered in the latest improved machines. Like the potato crusher it is surrounded by a fixed case, with an opening for the hopper, through which the beets are carried to the teeth of the quickly revolving drum; the irregular form of the beets often leads to a choking of the hopper, and sometimes they are so smooth that they glide upon the teeth of the drums without being reduced, unless some pressure is applied. In the old machines in connection with the hopper, which was situated on the side of the grater, there was a broad tube horizontally placed, into which the beets fell one by one from the hopper. In this tube was a

wooden lever, with which the workman pressed the beets upon the grater. Recent improvements in the crusher consist in the proper adjustment of this pressing arrangement. It is now made of metal instead of wood, and instead of being worked by hand, its action is now effected by machinery. One form of the machine used in the French factories is shown in fig. 607. A is the cylinder, the case of which is removed in order to show the teeth of the grater. It consists of a great number of saw

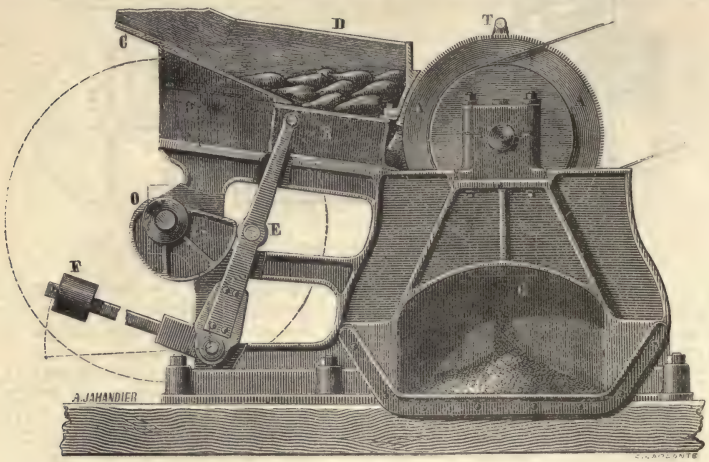


FIG. 607.

blades, each of which lies between and is held fast by two iron bands, the teeth of the grater being about $\frac{1}{12}$ inch above the bands. The cylinder has a diameter of about $2\frac{1}{2}$ feet, and a length of $4\frac{1}{4}$ feet, and has a motion communicated by the strap of about 1000 revolutions per minute. Above the cylinder, and inside of the case, there is a tube T, through an opening in which water is constantly sprinkled upon the cylinder in order to keep the teeth of the grater free, and to thin the pulp. The beets are thrown upon the inclined plane C, and carried to the body of the hopper D, where they are caught in the opening of the pressing apparatus and carried to the grater. The presser B, which in the cut is shown at one limit of its action, has a backward and forward motion caused by a double-armed shaft turning upon the point E in the following manner. The excentric O, turning upon its axis, at a certain point strikes the upper part of the shaft, and drives it as far forward as the position shown in the cut, and at the same time the presser, which is united with it, is driven to the one limit of its action. The excentric continuing its revolution ceases to be in contact with the shaft, and then the weight F attached to the other end of the shaft becomes operative, and causes it to turn in the opposite direction. This motion brings the presser back to the position indicated by B′, the lower opening of the hopper becomes free, and another quantity of beets are brought upon the presser. The excentric still in motion, again meets the upper arm of the shaft, drives it forward, and forces upon the grater the beets which are in front of the presser. The track of the presser is about 1 ft. 2 in. in length, and the excentric makes seven revolutions in one minute. The more rapid the movement of the cylinder and the slower that of the presser, the finer is the resulting pulp. At the lower edge of the box in which the presser works is an adjustable bar which connects the box with the grater. It is so placed that it almost touches the teeth of the grater, and the nearer it comes to the grater, the finer is the pulp, as it prevents coarse pieces which have been torn off and the outer rind from passing into the pulp. The fine pulp is thrown upon this bar, and falls at G into a suitable receptacle, under the grator. Each grater has four pressers about 10 in. in breadth, and these dimensions are sufficient for working up 250 tons of beets daily.

The graters of the German sugar manufactories differ from those of the French in being smaller, on which account they are more easily managed and more durable. The drum or cylinder of the German grater is only about half the diameter, usually 24 or 26 inches, and each is double, corresponding to two pressers. The drum consists of an iron frame formed of two disks and a shaft passing through the axis; the shaft has a driving strap wheel at each end, and a third upon the shaft between the disks,

dividing them into two courses. Two rings are cast upon each of these wheels, forming a groove. In fastening the teeth a clamp of seasoned wood is placed in the circular depression thus formed; then a saw blade is placed in position, and other clamps and saw blades are placed alternately until the whole case of the drum is fitted. The wooden clamps swell through absorption of moisture, and thus keep the saw blades secure in their position.

Sometimes the teeth become bent by the strong pressure, and unfitted to furnish a good pulp. The cylinder is then lifted from its position, and reversed so that it revolves in the opposite direction; the teeth then take hold of the beets and furnish a good pulp. The turning may be repeated until the teeth have been almost completely worn away, when a reserve drum is placed in the grater, the other being taken apart, and the teeth sharpened.

Champonnois' beet grater has been lately introduced into many of the French factories. The advantage which it possesses over the ordinary grater is that it furnishes a uniform pulp, entirely free from irregular pieces. The apparatus is very similar to the potato grater described on page 766, the only difference being that it is adapted to the larger size of the beets, and to the different quality of pulp required. If the pulp of the beets is too fine, it is not so easily pressed and partially passes through the pores of the pressing cloth. The dimensions found most effective for both purposes are as follows:—

	Champonnois' Beet grater	Potato grater
Interior diameter of the cylinder	15 in.	12 in.
Length of the saw blades	$9\frac{3}{4}$ in.	$7\frac{7}{8}$ in.
Number of revolutions of the shaft per minute	700–750	900–1000
Length of the teeth	$\frac{1}{25}$ in.	$\frac{1}{50}$ in.
Width of the opening between the saw blades	$\frac{1}{8}$ in.	$\frac{1}{25}$ in.
Length of these openings	$9\frac{3}{4}$ in.	$7\frac{7}{8}$ in.

A grater of these dimensions, having the speed above given, works up 62 to 65 tons of beets in twenty-four hours.

In using Champonnois' grater or crusher, it has been found that very hard incrustations form in a short time about the perforations through which the pulp escapes. These perforations are only about $\frac{1}{8}$ inch in width, and become completely stopped up in six or seven days. Payen found that these incrustations consisted partly of crystals of calcium oxalate and partly of cell residues. They may be easily removed by introducing a small brazier, containing a few glowing coals, into the hollow of the grater. The heat causes the concretions to shrivel up, and they may then be brushed away or removed with a fine steel knife.

In this way a fresh grater is run for five days. During the succeeding three days the cylinder has to be reversed every twelve hours, so that the teeth which are now becoming shorter may meet the beets from the opposite direction. During the following two days, the cylinder has to be reversed every six hours, after which the cylinder must be removed and replaced by a freshly sharpened one. The reversal of cylinders takes up about ten or twelve minutes.

The reduction of beets is considerably facilitated by the constant flow of a stream of water through the hollow shaft. The pulp thus thinned with about 15 to 18 per cent. of water, passes far more readily through the perforations of the cylinder, whilst the water added sets up an osmotic action with the unruptured cells, and thus a portion of the juice is secured which would otherwise be lost.

The dilution of the pulp is of great advantage in obtaining the whole of the juice, as will hereafter appear. For this reason, frequently much more water is used than stated above. But as the evaporation of the water added involves expense, it must be considered how far this expense is covered by the increase in sugar. Besides the cost of the fuel, the relative value of the raw material affects the practice on this point. If the French manufacturer fails in securing a portion of his sugar, although he thus loses a part of his raw material, the residue has more value as fodder. The German manufacturer working with raw material made more expensive by a heavy tax endeavours to obtain the greatest possible amount of sugar, and uses with 100 parts of beets 30 or even 50 parts of water.

Obtaining the Juice by Pressure.—In the separation of the juice from the pulp by pressure, the hydraulic press is generally used. This consists of a pump by which water is driven into a closed vessel, containing a movable piston or shaft that bears the table of the press. In proportion as water is driven into the vessel, this piston is raised. Opposite the movable table is a stationary one, and the substance to be pressed is placed between the two; the whole pressure exerted upon the water of the vessel by means of the pump can thus be transferred to the matter to be pressed. Fluids which are incompressible transmit a pressure exerted upon them equally in

every direction. The pressure exerted by the press bears the same relation to the power employed as the area of the cross-section of the press cylinder bears to the area of the cross-section of the pump piston. The power remaining the same, the effect will be greater the smaller the area of the pump piston, and the greater that of the press shaft.

Whilst the pulp is rich in juice, it flows away rapidly under a slight pressure. At this point of the work therefore but little force is needed, and a pump with a piston of proportionately greater section is used to drive water into the vessel. When however a certain quantity of the juice has been removed, the force available by means of this pump is no longer suitable, for upon increasing the power applied to it, the resulting pressure is so sudden, that the elasticity of the pulp would burst the covering in which it is being pressed before the juice could flow out. To avoid this, another pump with a considerably smaller piston is used. The action of this is slower, but all the more powerful. Thus, if the areas of the two pump pistons are to each other as 100 : 1, the area of the press piston and the working power remaining the same, the force exerted by the smaller pump will be one hundred times greater than that of the larger.

These pumps are so arranged that at first both work together; but as soon as the maximum effect for which it was designed is attained, the larger one ceases working and the smaller alone remains operative. This is allowed to work until the water in the tub of the press is under a pressure equal to 200 to 250 atmospheres. This pressure is continued as long as the pulp yields any juice, and then the water is run off from the press to the reservoir, the press piston with the table attached sinking in proportion as the press is emptied. The machine may then be emptied and freshly filled.

In order to press the pulp as produced by the grater, it is necessary to surround it with a covering that will allow the juice to flow freely through and retain the marc. Square cloths of very strong woollen texture are generally used for this purpose. Formerly several thicknesses of sacking were employed, but this material has now quite gone out of use. It had no advantage over the cloth, but the disadvantage of being more difficult to clean. The cloths are filled with the pulp upon the packing table at the press. This table is made of sheet iron, and has a rim round it; on one side of it there is a channel which allows such juice to run off as collects during the packing process. Upon this packing table is laid first a metallic plate of the same size as the pressing table; above this is placed a sheet-iron frame or shape, about ¾ inch in height, and the whole is covered with the press cloth. With a scoop about five or six pounds of the pulp is then thrown into the depression formed in the sheet-iron frame, then levelled, and the edges of the cloth thrown over it. Upon this is laid a second plate, and another cloth is filled in the same manner, so that at last there is a series of layers of pulp enclosed in cloths, and separated from each other by metallic plates. A portion of the juice now flows away in consequence of the pressure exerted by the mere weight of the metallic plates. The pile of alternating metallic sheets and layers of pulp is next placed upon the table of the press, and when the press is filled the pumps are set in operation. As the pressure is applied, the juice flows over the metallic borders, and along the surface of the pressing table, which is surrounded by a rim, and provided with an outlet pipe connected with a tube through which the juice is conducted to a proper receptacle.

The pulp possesses considerable elasticity, and offers so strong a resistance to the pressure, that, if too great quantities of pulp were to be operated upon at one time, the cloths would burst before the whole of the juice was separated. The layers of pulp are therefore made thin and metallic plates placed between them, so that the pressure may be uniform throughout the entire mass.

When the juice ceases to flow, the pressing table is lowered and the press is emptied. The cloths are found to contain beet fibres pressed into a very compact form, but still holding juice. The residue is therefore taken out of the cloths and either immediately used for fodder, or subjected to a second pressure to obtain the remaining juice, after having been again converted into pulp by the addition of water.

Various machines have been constructed for the purpose of reconverting the press residue into pulp. The so-called mashing machine of Fesca consists of a horizontal iron trough in which is a shaft furnished with a great number of knives arranged spirally. The knives cut up the press residue, and water being added, knead it into a stiff paste. This machine does not seem to be much used. Schlickeysen's machine, which is constructed after the pattern of the well-known clay pugmill, has met with much approval. It consists of an upright iron cylinder in which is a shaft furnished with strong arms inclining downwards; at the bottom of the cylinder is an opening for the escape of the pulp. The press residue is thrown from above through a funnel into the cylinder; at the same time water is poured on; the material being caught

by the moving arms of the shaft, becomes reduced, and escapes as pulp ready for a second pressing.

Beet juice is a tenacious sticky liquid in proportion as it is rich in sugar. Owing to its viscidity, it is impossible to extract more than a certain portion of the juice, the rest remaining in the residue, notwithstanding the strongest pressure. The better the quality of the juice, the greater is the proportion of juice which remains behind. When, by the addition of water, the juice is rendered thinner, it is less tenaciously held, and may be more completely separated from the press residues by pressure. Good beets with the strongest pressure yield about 80 per cent. of juice, and 20 per cent. of press residues, the latter containing 4 per cent. of pith and 16 per cent. juice; one fifth of the entire quantity of juice would therefore remain in the press residues. By the addition of water this loss is much diminished, because it can be more completely pressed; so that, instead of 20 per cent. only about 17 per cent. of press residue is left; further, the juice left in the residue is no longer a concentrated but a diluted juice, and consequently not only less in quantity but poorer in sugar.

The effect of thinning the juice may be shown by a few simple examples. Take, for instance, the case where beets of the following composition are used:—

Sugar	13 per cent.
Refuse	4 „
Water and non-saccharine matter	83 „

If these beets be subjected to pressure without the addition of water, until 20 per cent. of press residue is left, the residue will be composed of refuse and of 16 parts of juice in which sugar and water are present in the same proportions as in the beets themselves, thus:—

Sugar	2·2 parts by weight
Refuse	4·0 „ „
Water, etc.	13·8 „ „

Since therefore 100 parts of beet contain 13 parts of sugar, and 20 parts of such press residue would contain 2·2 parts of sugar, there would be in this case a loss of 17 per cent. of the whole of the sugar.

If 20 parts by weight of water be added to every 100 parts of beets, this will produce 120 parts of pulp of which the composition will be as follows:—

Sugar	13 parts by weight
Refuse	4 „ „
Water	103 „ „

This thin pulp may be easily pressed until not more than 18 parts of residue remain from every 100 parts of beet. But the relative proportions of sugar and water are no longer the same in this residue as in the beets, but are the same as in the diluted pulp.

The composition therefore of the 18 parts of the residue will be as follows:—

Sugar	1·6 parts by weight
Refuse	4· „ „
Water, etc.	12·4 „ „

The loss in sugar is therefore reduced to 12 per cent. of the whole.

Still further dilution is attended by a corresponding gain in sugar. If, for example, 50 parts of water be added to every 100 parts of weight of beets, this will give 150 parts by weight of pulp, which will consist of:—

Sugar	13 parts by weight.
Refuse	4 „ „
Water, etc.	133 „ „

As the process of obtaining the juice is easy in proportion as the pulp is thin, the pressing may be conveniently carried on until 100 parts of beets leave only 17 parts of residue, which will consist of:—

Sugar	1·2 parts by weight.
Refuse	4 „ „
Water, etc.	11·8 „ „

Thus the loss in sugar in a single pressing would be reduced 9 per cent. upon the whole.

The yield of sugar is still more favourable when the residuum from the first pressure is thinned with water and pressed a second time. If a pulp obtained without any water being poured upon the grater, be subjected to a first pressing, and this pressing be only sufficient to yield 70 parts of juice and 30 parts residue from every 100 parts of beets, the residue would then contain:—

Sugar	3·5 parts by weight.
Refuse	4· ,, ,,
Water, etc.	22·5 ,, ,,

If now to these 30 parts of residue, 30 parts of water be added, the resulting 60 parts of pulp may be pressed without difficulty, so as to obtain 27 parts of juice and 17 parts of residuum, the composition of this residue will be as follows:—

Sugar	0·8 parts by weight.
Refuse	4· ,, ,,
Water, etc.	12·2 ,, ,,

This would be a loss of only 6 per cent. upon the whole of the sugar. By proper management this loss in sugar can be still further reduced. If, for instance, in reducing another lot of beets the 43 parts by weight of thinned juice, which had been obtained by a second pressure, be caused to flow upon the grater instead of water, the product will be a pulp which is thinned by means of diluted juice. Thus the pressing of this new pulp would be facilitated, there would be a less amount of residuum than before, and this would contain a smaller quantity of sugar. If this residue be a second time subjected to pressure, nearly all the sugar is obtained.

In these calculations it has been assumed that when water is applied it is completely incorporated with the juice; this takes place more perfectly if, in the grating process, the individual cells have been thoroughly ruptured, as it is only from the cells that have been actually torn open that the juice can issue freely and mix with the water. When unruptured cells come into contact with the water, there is of course an interchange of the constituents of the juice with the water by diffusion, but this process is a slow one. Although it may not be possible to attain a complete mixture of the juice and water in the short time which intervenes between the application of water and the pressing, yet the effect of the dilution is always considerable, especially if the pulp be pressed a second time.

As soon as the juice leaves the cells it is liable to many prejudicial changes. Fermentation occurs in consequence of the action of the ferments contained in the air; acids are formed and a considerable formation of mucus takes place, which is distinctly observable when fresh juice is exposed for a short time to the action of the air. This formation of mucus may take place to such an extent that the whole of the juice is changed to a jelly-like mass. To prevent this the greatest expedition should be used in working up the juice, but especially the greatest cleanliness should be everywhere observed. If the apparatus is left unused even for a short time it should be thoroughly washed with water, as the standing juice is not only subject to chemical changes, but it is a focus of fermentation of every kind. On this account the press cloths must be thoroughly cleansed after they have been used only a very short time. The cloths become covered with mucus every few hours, and no longer allow the juice to flow freely through. They must then be at once removed and washed, clean ones being employed in their place.

The press cloths are subject to a good deal of wear and tear, and are soon destroyed; hence attempts have been made at different times to construct an apparatus which should render their use unnecessary. It has been proposed to place the pulp between two endless wire tissues, and to press these together between rollers. This plan, however, has not yet met with much acceptance.

The juice as it leaves the press is not quite clear, but is more or less contaminated with fibrous matter that has been forced through the pores of the press cloths. Formerly no notice was taken of this, but it has now been discovered that the pectic substances upon treatment with lime become changed into metapectic acid, which hinders the crystallisation of the sugar. These fibrous constituents are therefore removed by filtration of the juice; for this purpose long rather narrow linen sacks are used, which hang freely; into these the juice is poured, and it leaves the sacks a clear liquid, the fibrous matter remaining.

Obtaining the Juice by Centrifugal Force.—The beet pulp is prepared in the ordinary way by rasping, and is placed in a centrifugal machine like that used for raw sugar, but of larger dimensions and having the rotating machinery underneath the drum. The paste falls from the rasper into an iron funnel, suspended from a pair of iron rails, and having a capacity exactly corresponding to that of the drum. Immediately underneath the rails stand the centrifugal machines in a row; the funnel when filled is pushed forward until it is exactly over the already revolving drum, a slide at the lower end is opened and the paste falls into the drum. Here it is immediately flung against the periphery; the mark is retained whilst the juice flows through. As, however, the pressure is not so great by far as that exerted by the hydraulic press, the mark retains after this treatment much more juice, and consequently sugar, than when the press is used. In order to recover this sugar, water

is allowed to play upon the partially exhausted paste in the drum from a very fine rose. Under the influence of the centrifugal force, the water percolates through the paste driving the juice before it.

Obtaining Juice by Maceration.—The apparatus introduced by Schutzenbach consists of twelve shallow cylindrical vessels placed terrace-like, and communicating with each other by a pipe, similar to the apparatus used for lixiviating crude soda (see p. 263). A pipe that can be closed by a valve passes from the bottom of the upper vessel and opens over the vessel next underneath. Each vessel has besides a tap at the bottom through which the entire liquid contents can be run off into a trough. Each vessel is provided with a false bottom, consisting of a fine wire sieve, through which none of the paste can pass. In the upper part of the vessel is a second false bottom of perforated sheet iron. The entire capacity of the vessel is about 36 cubic feet; the space from the true bottom to rather over the upper false bottom will hold 94 gallons of water and 66 gallons of paste. The paste is placed between the two false bottoms, where by means of a stirrer it is intimately mixed with the incoming water.

The stirring machinery consists first of an iron bar directly underneath and resting against the upper bottom; from this bar numerous iron teeth, 6 inches long, project downwards. Through a circular opening in the middle of this bar passes a vertical shaft that revolves in a socket at the bottom of the vessel, and is connected above with the driving power common to all the shafts. Between the two false bottoms this shaft supports a horizontal iron bar, almost as long as the diameter of the vessel. To this are fastened vertical bars, arranged so that the upward directed half passes between the before mentioned teeth, whilst the half directed downwards reaches to within an inch of the lower bottom. The shaft also supports above each of the two bottoms an arm set with brushes, the upper one serving to break up the scum and the under one to purify the sieve bottom. All twelve vessels are arranged in a similar way, and can easily be connected with or disconnected from the motive machinery.

The upper vessel is first two thirds filled with cold water, into which sixty-six gallons of paste have been thrown, the upper false bottom is put on, the stirrer is put in motion, and just so much water is added as will exactly cover the upper bottom. After the paste has been five minutes in contact with the water the valve of the pipe that connects the first vessel with the second is opened, and water is allowed to flow upon the upper stage of the first vessel which drives the juice out and forward into the second vessel. The flow of water is kept up until the juice in the second vessel equals the quantity of water present in the first vessel at the commencement of the operation; the stirrer is then set going, sixty-six gallons of fresh paste are added, the false bottom is put on, and the paste and juice are left in contact five minutes. The third vessel is then filled by opening the overflow pipe connecting it with the second vessel, and allowing more water to run into the first vessel; this drives the thin juice in the second vessel, which has already been in contact with two separate quantities of paste, forward into the third vessel. This operation is repeated until eight vessels have been filled.

By this time the juice has attained nearly the same concentration it has in the paste; it is therefore run off through a cock at the bottom into a trough that conducts it to the montejus, by which it is raised to the juice reservoir. The paste in the first vessel being now exhausted, fresh water is allowed to flow into the second vessel, which then becomes the first of the series, whilst the ninth being fitted with fresh paste after five minutes yields a second portion of finished juice. Thus, after the operation has once been started, a vessel full of juice is obtained and a portion of paste is exhausted every five minutes. When saturated juice has been drawn off from the twelfth vessel at the foot of the terrace, the next quantity of juice passing into it is run off through a trough into a small cistern, from whence it is pumped into a reservoir standing higher than the first vessel, which has meanwhile been filled with fresh paste, and into which it can then be run. A complete circle is thus set up, eight vessels being always at work, the four intervening ones being meanwhile emptied and cleaned, the water being run off through the cock at the bottom, and the mark withdrawn through an opening just above it, and submitted to slight pressure to free it from the large quantity of absorbed water.

Before the clarification, the juice always requires to be filtered, as it is impossible completely to prevent the passage of fibre through the sieve bottom.

Obtaining the Juice by Diffusion.—When a living cell or a number of uninjured cells are placed in water an interchange of the cell contents with the water is always set up: water passes through the cell membrane and protoplasm, and the matters dissolved in the cell juice pass through into the water. This interchange continues until the oppositely attracting influences are balanced, and the liquids inside and outside the cell have an equal concentration. The protoplasm and cell membrane present a certain resistance which varies very much according to the chemical compo-

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sition and physical properties of the body. Many bodies pass readily from the cell into the water, others slowly, and some not at all. All bodies that are capable of taking the crystalline form pass easily through the cell membrane, whilst those that are not remain in the cell. Thus when a cell containing juice rich in sugar, which is crystallisable, is laid in water, sugar passes out into the water and water enters into the cell, until the concentration of the cell juice and that of the liquid outside the cell are equal. This is known as the process of diffusion; sugar is a diffusible or crystalloid body. On the other hand, with a cell the juice of which contains albumen in solution, under otherwise equal conditions, the albumen does not pass out from the cell into the surrounding water. The albumen is not diffusible, not having the power of crystallisation; it is a colloid. Finally, from a cell enclosing juice containing sugar and albumen only the diffusible sugar passes into the water whilst the albumen is retained. The power of diffusion therefore can be used to separate these bodies from one another, and to effect a clarification even in the cell.

The diffusion takes place very unequally, according to the conditions of the cells. In the living cell the process goes on slowly, the diffusible matters being held so closely during the life of the cell that they cannot penetrate the protoplasm and membrane. But as soon as the life of the cell is destroyed through frost and a rapid thaw, or heating to 40° or 50°, the diffusion goes on rapidly.

Upon these facts the method introduced by Dombasle, and afterwards improved by Robert, is based. By suitable arrangements, this method effects a complete removal of the sugar, and the juice is moreover obtained almost of the same concentration as that in which it exists in the beet.

If 100 parts of beet, containing 96 parts of juice with 14 parts of sugar, be brought together with 60 parts of water, the result after diffusion is 156 parts of juice, containing 14 parts of sugar, or a 9 per cent. juice. If from this juice be taken as much as the quantity of water used, *i.e.* 60 parts, and this be placed with 100 parts of fresh beet, as the added juice already contains 5·4 parts of sugar, there will be after diffusion 156 parts of juice, with 19·4 parts of sugar, or a 12·5 per cent. juice. 60 parts of this juice containing 7·5 parts of sugar placed with another 100 parts of beet will give 156 parts of juice with 21·5 parts of sugar, or a 13·8 per cent. juice; this would consequently be equal to that in the juice.

If the beet from which the first juice was withdrawn, which still contains $14 - 5{\cdot}4 = 8{\cdot}6$ parts of sugar, be again treated with 60 parts of water, 156 parts of juice are obtained with 8·6 parts, or 5·5 per cent. of sugar. If 60 parts of this juice be again replaced by 60 parts of water, the resulting juice will still contain 5·3 parts, or 3·4 per cent. of sugar. It will be evident that by continuing this treatment a point is reached when the sugar of the beet cells is almost completely replaced by water. The result of the last treatment, being almost pure water, is used with the beets still containing 1 per cent. of sugar, and the yield from this is used with beet containing double that quantity, and this is repeated until the most concentrated juice is obtained.

The apparatus used by this method consists of a small dividing machine and the diffusers. In this case the beets are not reduced to a paste, but by means of a special machine they are cut into small very thin uniform slices. The thinner these are, so that the cells may come into immediate contact with the water, the more uniform will be the diffusion and the more completely will the juice be obtained.

The diffusers are tall iron cylinders, eight or ten of which are combined together to form a battery. Above and below at the side, they are provided with a large man-hole for the introduction and removal of the slices. They are connected with each other by pipes, that pass from underneath one into the upper part of another into which they discharge through a rose. A second series of pipes connects each separate cylinder with an elevated water reservoir. A third series of pipes passes from the bottom of the cylinders to a warming apparatus situated between the reservoir and the cylinder, and containing a pan that can be heated by steam. This pan is sufficiently large to hold the quantity of liquid—water or juice—required for the filling of the cylinder. In working with a battery of eight diffusers, it is usual to use 60 parts of water or juice to each 100 parts of beet; with a larger number, less liquid will suffice.

In commencing operations, the pan is filled with water which is heated to boiling. The hot water is allowed to flow slowly into the first cylinder, and at the same time the slices of beet are thrown in, until the cylinder is completely filled with beet slices and liquor; the cover of the man-hole is then closed, and the whole is allowed to stand for twenty minutes. The temperature should reach 50° in order to kill the cells and thus allow the diffusion to go on rapidly. The temperature of the water in the pan must therefore be regulated according to the temperature of the beet, and the proportion of water used. After twenty minutes, the valve which connects the first

cylinder with the water reservoir and the heating pan is opened. As the water reservoir stands at a considerably higher elevation than the other portions of the apparatus the water flowing in drives the juice through the pipe commencing at the lowest part of the cylinder into the heating pan. When this is filled with juice, the valve is closed and the juice is heated, whilst the first cylinder filled with water is allowed to stand under the pressure of the column of water. From the heating pan the juice is run into the second cylinder, which is also filled with slices; when full the second cylinder is closed and allowed to stand twenty minutes. The connection between the first and second cylinders and the water reservoirs being then opened, fresh water enters the first cylinder and drives the juice there forward into the second cylinder and the juice from the second cylinder into the heating pan. When the pan is full, the connection is closed and the first and second cylinders remain under water pressure. The hot juice from the second cylinder is then run into the third, where it is used as before, for heating a fresh quantity of slices of beet. After being in contact with three portions of fresh beet the juice is sufficiently concentrated. It is then passed through a special pipe into the defecation pans, which are of a capacity corresponding with that of the cylinders.

After the juice has been run off, the connection between the second and third cylinders is opened. Water again flows into the first cylinder, and drives the thin juice into the second, and the contents of the second into the third cylinder. After twenty minutes the third cylinder is connected with the heating pan, and for the fourth time fresh water is let into the first cylinder, which drives the contents of each cylinder successively into the next. The juice from the heating pan meets with fresh beet in the fourth cylinder; it there becomes sufficiently concentrated and is drawn off, the cylinder being again filled from the third. In the same way the other cylinders are filled, until all are in connection. By the time the contents of the seventh cylinder are passed into the eighth the beet slices in the first cylinder are perfectly exhausted of sugar. The second cylinder is then connected with the water reservoir, the valve between the first and second cylinders is closed, and the fluid contents of the first, consisting only of pure water, are run off, and the exhausted slices are removed. The eighth cylinder is then connected with the first, and the first is filled with fresh slices of beet and juice from the eighth. Meanwhile the second cylinder has become exhausted; the water pressure is therefore applied to the third; the second is connected with the first, and so on.

In working with a battery of twelve cylinders the method is essentially the same. Either a larger quantity of beet, or the same quantity with less water, can be exhausted in the same time; but the usual plan is to have two batteries of eight diffusers each, and to manage so that whilst one is under pressure the other is being freshly filled.

Of all the methods of obtaining the juice, diffusion is undoubtedly the most to be recommended. The apparatus is the simplest, least costly, and undergoes scarcely any wear; the building not having to sustain the violent shaking of the raspers can be more simply constructed; the batteries do not take so much room as the presses; press bags are not required; the juice is of at least equal concentration, and can even be obtained less dilute than by other methods; whilst the loss of sugar is not greater than when presses or the centrifugal apparatus is used.

It has been sought to simplify this method by using instead of the batteries a single apparatus, in which by a mechanical arrangement a stream of water and slices of beet are carried forward in opposite directions. Thus at one end the fresh slices are introduced, and the concentrated juice flows out, while at the other end the exhausted slices are thrown out.

Only one difficulty stands in the way of the diffusion method, the condition of the residue, or exhausted slices. The residue from the hydraulic press is comparatively free from water, containing 30 to 33 per cent. of dry substance. From the ruptured cells the juice can be expressed, but not so from the undestroyed cells after diffusion. These are filled with water, and contain at most 8 per cent. of dry substance, or much too little to allow advantageously of its use as fodder. The adherent water can be separated by simple pressure, but that in the cells is expelled with difficulty. Several presses have already been constructed with this object.

Obtaining the Juice from dried Beets.—Attempts have long been made to work the beets in the dry instead of the fresh condition, the advantage being the more easy transport of the beets, and the extension of the working season through the entire year. On the other hand, it has its disadvantages. The sugar must still be exhausted from the dried beets with water, and the quantity of liquid to be evaporated is great. Moreover the roots in drying are subject to many injuries. If they are overheated a portion of the sugar is destroyed; whilst if they are imperfectly dried, they form a favourable basis for fungoid vegetation, by which also sugar is decomposed. These

disadvantages appear to outweigh the advantages, and but few manufacturers have adopted this method.

After gathering the beet roots they are washed and cut by machinery into long rectangular pieces, and dried in a kiln. The dried pieces contain about 3 to 5 per cent. of moisture, and with care can be preserved in a perfectly dry room for a long time. For obtaining the juice an apparatus similar to that used in diffusion is used. Fourteen cylinders are connected with one another by pipes to form a battery. The pieces of beet are placed in the cylinder, covered with half per cent. of their weight of calcium hydrate, and then boiling water is poured over them. The juice passes from one cylinder to another, and acquires a concentration of 36° to 40° of the saccharometer; it is then run into the defecation pan, where it is heated only to 90°. The further working is the same as in the other processes.

The difficulty of transporting the beet root has given rise in one or two places in France to the separation of the processes, the juice being obtained on the spot where the beets are grown, and then conducted by pipes to a central manufactory to be worked up. The juice is mixed with 1 per cent. of lime to preserve it, and is then driven by powerful pumps through the pipes into a large reservoir in the central manufactory. The pipes are laid about three feet below the surface of the earth, the juice being thus protected from freezing.

Clarification of the Juice.—The process of defecation or the clarifying of the juice has for its object the removal of such constituents as are coagulated by heat or precipitable by lime. Lime enters into combination with any free acids that may exist in the juice, saturates the acid salt, and combines with gum, albumin and casein, forming an insoluble precipitate. It also converts the fatty substances into insoluble lime soap, and precipitates the colouring matter. Magnesia, ferric oxide, and phosphoric acid are separated in an insoluble form. The salts of the organic acids are decomposed, and the bases with which they were combined, such as ammonia, potash and soda, are liberated, while the excess of lime combining with sugar forms sugar-lime. If the juice contains grape or fruit sugar, this also enters into combination with lime, but the compound quickly decomposes, colouring the juice yellow or brown, according to the quantity present. Thus the lime affects the most diverse constituents of the juice, and the non-saccharine constituents could be almost completely separated by its use, if all the reactions took place in this simple way. Various secondary processes, however, hinder the clarification from being as complete as might be expected. The albumen contained in the juice becomes so much changed by the action of the alkalies set free, that a part of it is dissolved, and cannot be removed. The lime salts too, which are insoluble in pure water, are dissolved by water containing sugar, and the liberated alkalies partly replace the lime in the lime salts of the organic acids, forming the same salts which had been previously decomposed by the lime. The object of further operations is to remove these substances.

The defecation and evaporation of cane juice were formerly carried out in a very rough manner in a series of cauldrons standing side by side, and heated by a common fire. The cauldron furthest removed from the fire was the defecation pan and in this a small quantity of milk of lime (0·2 to 0·3 per cent.) was added to the juice. The impurities rose to the top as scum which was removed with a ladle.

By precipitating juice having a specific gravity of 1·060, or 15° sacchar, with cold lime water, Avequin obtained per 1,000 parts 38·36 parts of dried scum, which contained:—

Cerosin	7·15
Green colouring matter	1·50
Albumin and traces of cellulose	5·56
Calcium and magnesium phosphate	15·70
Calcium carbonate	2·30
Silica	6·15
Ferric and manganic oxide	traces

The juice from a cane grown in new land gave 40 to 70 parts per 1,000 of dry scum; that from a quite ripe cane grown upon land that has been longer in culture yielded a smaller amount of scum.

After the removal of the scum, the juice is transferred by means of a ladle into the second vessel. Here during evaporation, a fresh scum is formed that is continually skimmed off and returned to the first vessel, which has been meanwhile filled with fresh juice. After becoming clear, the juice passes into the third vessel. Here the colour and condition of the juice are noted, and, if necessary, a small quantity more lime added, and it is then skimmed until all the impurities have been removed. In the fourth vessel it is brought to the consistence of a syrup, and finally in the fifth

the boiling is finished when the boiling juice throws up bubbles that burst with a crackling noise.

The original cast-iron hemispherical vessels have been replaced by flat pans having perpendicular sides, arranged terrace-like one above another, but still heated by one fire. The pans are therefore not set firmly, but so that each can be raised at one end, and its contents emptied into the next lower pan. Pans of this kind are termed swing pans. The combustion products passing from under the last pan are conducted into a tubular boiler and the steam is used for heating the apparatus in which the final concentration takes place.

Whatever form of apparatus may be used, however, the boiler over a bare fire is always extremely imperfect. The juice undergoes change by the long contact with atmospheric air, and by overheating a larger quantity of the sugar is converted into a non-crystallisable coloured product, called caramel, so that a disproportionately large quantity of syrup and but little crystallisable sugar is obtained. In order to avoid this, apparatus heated by steam is being more and more used. By large capitalists the steam apparatus of Rillieux is used; while those of smaller means use apparatus in which, though not provided with the aarangement for producing a vacuum, the heating of the concentrated syrup is effected by steam. The kinds of apparatus used in the French colonies are in principle similar to those used in the concentration of dextrin solutions. Two kinds of apparatus, Wetzel's and Bour's, are especially in use.

Wetzel's apparatus consists of a half cylinder having double sides. It has a stirring arrangement formed of a hollow shaft, which is fitted with two lenticular shaped bodies, connected one with the other, by numerous pipes. Steam is passed into the space between the inner side of the cylinder and the jacket, as well as into the hollow shaft of the stirrer. The agitator is set in motion, and through the considerable surface it presents, the heat is rapidly communicated to the liquor and the evaporation rapidly effected.

The apparatus of Bour has a similar arrangement; it is shown in figs. 608 and 609. B is the juice-holder, having a semi-cylindrical bottom, and surrounded by a steam-jacket (c). The steam enters through the pipe (*a*), and passes off through *d*, into the

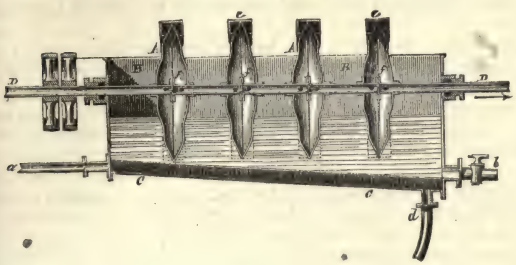


Fig. 608.

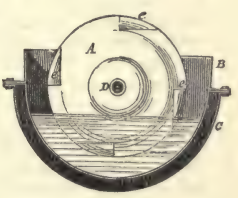


Fig. 609.

steam collector. The stirrer (A) consists of a hollow shaft (D), upon which are fastened four hollow bodies (*f f*). The steam goes in the direction of the arrows, but on its way must pass through the four bodies (*f f*). Each of these bear two cups, which dip into the juice, carry with them a portion, and upon becoming reversed, pour it out over the space filled with steam. The shaft is driven by means of pullies or a handle.

During the evaporation of the juice, there is formed on the side of the pan or cauldron a deposit, called in the colonies cal. It consists of almost pure calcium phosphate. According to an analysis by Avequin, it contains:—

Calcium phosphate	92·43 per cent.
Cupric phosphate	1·42 „ „
Calcium carbonate	1·35 „ „
Silica	4·75 „ „

The composition of the cal naturally varies according to the purity of the lime used in the defecation. The amount of copper salt depends upon the use of copper vessels in the evaporation. In order to remove it, the pans are heated after the removal of the juice to dryness; the adherent mass is thus rendered friable and can easily be removed with a chisel. In Rillieux's apparatus the deposit is not so dense, and can be easily removed with dilute hydrochloric acid.

The clarification of beet-root juice is carried on by very different methods. The older method and that which is still very much in use is as follows:—The clear juice is run into the clarifying pan, placed so that the juice can be conducted to it from the press or filters by means of inclined channels; or if this arrangement is not possible, the clarifying pan may be placed in the upper story of the building, so that the juice may flow from it to any other position required. To raise the juice, which must be done either now or at some other stage of the work, an apparatus called the monte-jus is generally used. This consists of a closed cylindrical iron vessel in the upper part of which terminate two pipes furnished with stopcocks. One of these cocks is used for filling the vessel with juice, and the other opening at the highest point of the arched lid is in direct communication with the steam chest of the boiler; a third pipe passes through the bottom of the apparatus, and is used for running off the juice to the clarifying pan or any other receptacle. The steam tube being closed the monte-jus is filled with juice. The juice tube is then closed and the cock of the steam tube opened. The steam admitted presses with the whole of its expansive force upon the surface of the sap and drives it through the pipe opening at the bottom of the apparatus into the clarifying pan or other vessel appointed for its reception. When the monte-jus is emptied the juice cock is again opened and the steam cock shut and the operation is repeated.

The clarifying pan is a circular boiler made of copper, the bottom of which is round, generally hemispherical. It is surrounded by a steam jacket, furnished with a pipe for the inlet of the steam, and another for carrying away superfluous steam and the water which has become condensed. For the purpose of heating the juice, steam is used either directly from a boiler, or more advantageously steam which has already been employed in driving the engine. The jacket must be strong enough to bear the pressure of steam of high tension, as the liquid in the pan has to be brought to boiling.

As soon as the pan is filled with juice, steam is let into the jacket, and the temperature raised as quickly as possible to 80°. The first effect is the separation of albumin, which coagulates at a temperature of 65°. When the thermometer indicates a temperature of 80° or 85° at the most, the flow of steam is lessened so that further increase of temperature may take place gradually. Lime mixed with water to a thin paste is then added, and well stirred up with the juice so as to cause a thorough mixture.

Directly the lime comes into contact with the juice, a considerable quantity of flocculent precipitate separates. The temperature is then gradually raised, causing the formation of more precipitate, which does not sink to the bottom, but floats as a scum of gradually increasing thickness upon the surface of the liquid; for this reason the process is known as the upward clarification process. The liquid is just allowed to enter into ebullition, and the steam is then shut off. If the operation has been properly conducted all the scum will now be found upon the surface and beneath will be a completely clear liquid. The scum contains almost all the colouring matter, and the previously dark coloured juice is now a clear yellow. If the liquid remains turbid after the boiling, or if the juice is not separated from the scum, the result indicates that not enough lime has been used, and in the next clarification the quantity of lime must be increased.

Two different arrangements of the pan are in use for separating the clear fluid from the scum; one consists of a tube passing through the bottom of the pan and jacket, which is closed by means of a valve during the process of clarification, and then carefully opened. The clear liquid is allowed to flow away, but as soon as it begins to be clouded by admixture of scum the valve is closed, and the scum is run off to the filter press, where it is completely freed from juice.

The other arrangement for the separation of the juice from the scum consists in a siphon which passes through the wall of the pan and enters the liquid below its surface, the short arm terminating at the bottom. The long arm opens outside the pan over a funnel connected with the juice reservoir, and governed by a stopcock. As the highest point of the siphon is below the surface of the liquid, the stopcock need only be opened to set it in motion; the clear liquid is allowed to run off, but the scum, the consistency of which will not permit it to escape, remains behind and is ladled out afterwards.

With reference to the quantity of lime which is requisite in clarification, nothing definite can be stated, because the amount of matter required to be removed varies greatly. Some kinds of beet contain much more non-saccharine matter than others. Those that have been well preserved too contain a less amount than those which become rotted in the pits, and the same beets contain less immediately after they are gathered than in the spring. All these considerations affect the use of lime, so that reliance must be placed entirely upon observation of the appearance of the juice, and sufficient

lime be used for the juice to be clear after boiling and no longer dark coloured. In general, however, it may be assumed that for 100 parts of beets by weight, half to three-quarter parts of lime will be required. The variation will generally be within these limits.

The clarified juice has a very alkaline reaction in consequence of the liberation of the bases, potash, soda, and ammonia (which escape in the boiling), and by the formation of sugar-lime. Since lime is only difficultly soluble in hot solutions of sugar, the formation of sugar-lime never exceeds a certain limit, even should an excess of lime be used, which should however be avoided. The alkalimetrical strength of ordinary refined juice represents an average contents of about 0·2 per cent. of lime. The alkalinity of the juice is of great importance for its preservation; fermentation and formation of mucus occurs only in acid or neutral juice, whilst an alkaline juice remains free from these changes. On this account the sap is never, even in the later processes, completely freed from dissolved sugar-lime.

Saturation.—Although a certain quantity of sugar-lime in the juice is requisite for its preservation, the amount present after clarification is too considerable to be profitably allowed to remain. It is true the lime would certainly be removed in the subsequent filtration through animal charcoal; but this would be at the expense of the quality of the charcoal, for when the charcoal is saturated with lime it is no longer capable of absorbing the substance for the removal of which it is chiefly employed.

As carbonic acid readily decomposes sugar-lime, it is now generally used for saturating the juice. The apparatus used for this purpose was invented by Kindler. It consists of an iron cylinder which is higher than it is wide. Some factories employ wooden vats, the sides of which are furnished with a spiral steam tube for heating the juice. At the bottom is a second tube or coil perforated along its surface for the purpose of admitting the carbonic acid. The large quantities of steam formed escape from the saturator through a funnel-shaped head-piece, prolonged so as to extend above the roof. In this head-piece a trap is fixed, through which the progress of the juice may be easily watched.

Carbonic acid decomposes not only the sugar-lime, but also a number of other sugar constituents precipitated from the juice by the lime; care must therefore be taken that only the clearest juice is saturated, and that all the scum remains in the clarifying pan. For this reason the first and last portions of juice, which are always contaminated with scum, are separated and added to the bulk of the scum that they may be filtered before being saturated.

The saturator being filled with hot clarified juice, steam is admitted into the heating coil, and the liquid heated to ebullition; carbonic acid is then introduced into the boiling juice by means of a force-pump. The boiling liquid has a great tendency to form a froth, and would be partly lost if the frothing were not prevented. This is effected by the addition of small quantities of fat, tallow, butter, or paraffin, which melt and form a thin layer upon the surface of the liquid, causing the bubbles of the steam to burst.

Production of the Carbonic Acid.—The carbonic acid used for saturating the juice need not be chemically pure. An admixture of other gases presents no further disadvantage than that a greater volume must be used, and that the carbonic acid thus diluted is not so readily absorbed as that which is pure. Pure carbonic acid produced by decomposition of carbonates with stronger acids would be much more expensive than a larger quantity of carbonic acid mixed with other gases.

A number of different kinds of apparatus are used in the preparation of carbonic acid gas, amongst which Kindler's furnace still enjoys considerable reputation. It consists of a small shaft furnace, at the grate of which a fire is kindled. As soon as this is in a lively flame, the entire shaft is filled gradually with fuel, generally coke, as free from sulphur as possible. The upper opening of the furnace is then completely closed, and a strong draught maintained by an air-pump, which drives the air through the grate, bringing it into contact with the red-hot fuel, the oxygen of the air combining with the carbon to form carbonic acid. The product of combustion containing nitrogen and steam is at once drawn off from the side of the furnace near the fireplace, in order to avoid the carbonic acid remaining too long in contact with the red-hot coke, which would cause the reduction of the carbonic acid to carbonic oxide, and consequent waste. The hot gas is then cooled by drawing it first through a chamber filled with pieces of limestone and pans of water, and then through a reservoir filled with water. The high temperature of the gas serves to expel a portion of the carbonic acid from the limestone, and any sulphurous oxide present, originating in the combustion of sulphur compounds in the coke, is retained. In passing through the water, the accompanying dust, ashes, etc., are removed. After the gas leaves this water tank, it passes into a suction and force-pump, and is by it forced either into a reservoir or gasometer, or, as is customarily the case, immediately into the saturation vessel.

In many factories at the present time, the production of carbonic acid and of lime are combined, and the furnace made use of is that shown in the figs. 610 to 612. Fig. 611 is a vertical section; fig. 612 is a horizontal section made on the line C D, at a height of about 2½ feet above the grate. Fig. 610 is a horizontal section through the line A B at the top of the flue.

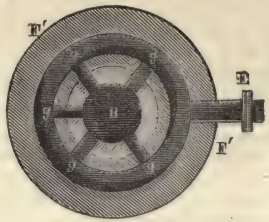


FIG. 610.

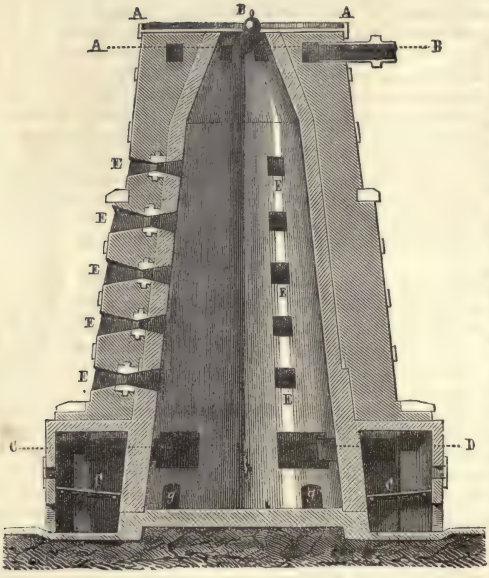


FIG. 611.

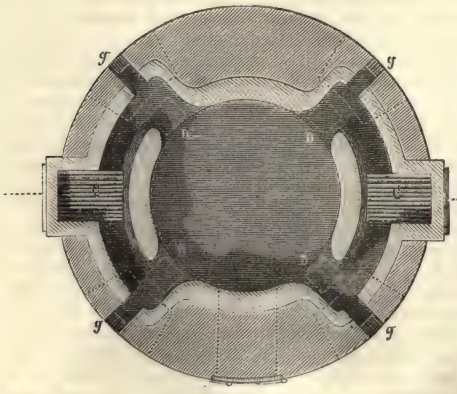


FIG. 612.

The furnace forms a cone, the greatest diameter of which upon the ground is about 11 feet, and the least diameter at the top is about 3 feet. A little way above the ground at the side of the shaft are two fireplaces, the grates of which are about 3¼ feet long, 2 feet 8 inches wide. These are provided with doors, by means of which the draught may be regulated. The flame does not enter the furnace immediately, but is broken by a fire bridge, as shown in fig. 612, and enters the furnace in two currents. A regular distribution of heat throughout the shaft is thus attained, the four openings of the two fireplaces being situated at an equal distance from each other. Around the furnace are five tiers of openings, each tier containing three, which are situated at an equal distance each from the other. These shut hermetically, but are used to observe the state of the furnace, and also for allowing air to enter if required; any choking of the furnace is removed through these openings with an iron bar. Above is the shaft, and the whole furnace is covered by a strong cast-iron plate, composed of three different parts. Beneath this plate at a distance of 1½ feet, there is a circular channel running round the whole of the upper part of the shaft (B), and this is in connection with the interior by means of fire linnet holes. This channel receives the whole of the product furnished by the combustion as well as the carbonic acid driven out of the limestone, and carries it away by means of the cast-iron pipe (F). The draught is supplied by a large force pump, which first collects the air, then the products of com-

bustion from the furnace, and afterwards drives these products to the place where they are required.

Such a furnace yields in twenty-four hours 6 tons of burned lime which requires upwards of 10½ tons of pure carbonate of lime in the limestone used. The limestone is broken into pieces about 10 cubic inches in size, and after the furnace has been set going, small quantities of these are thrown in at intervals of an hour, through three round holes in the upper plate, each 8 inches in diameter. As soon as the limestone is thrown in, the holes are closed by means of three large hollow balls (B, fig. 611), provided with handles. The holes are charged alternately so that the limestone may be placed as uniformly as possible in the furnace. About 3 cwt. of limestone is thrown into the furnace at a time, and with this limestone is mixed about 15 lbs. of coke. Beside this, about 30 cwt. of coke is used in the two fireplaces, making in all about 2 tons in the twenty-four hours. The 6 tons of pure lime in the limestone is combined with about 5 tons of carbonic acid, and the 2 tons of coke, if it were pure carbon, would produce nearly 7¼ tons of carbonic acid in the combustion. Theoretically, then, the capacity of the furnace would be equal to the production of about 12 tons of carbonic acid in twenty-four hours. But the limestone is not pure calcium carbonate, neither is the coke pure carbon, so that the actual amount obtained will fall considerably below this estimate.

The burnt lime is drawn out at the hearth of the furnace through the opening (*g g*) closed by iron doors. The carbonic acid drawn off by the pump is cooled by passing through a wide iron tube, which conducts it from the top of the furnace to a washing apparatus. This is shown in fig. 613, and consists of a cast-iron cylinder about 5¼ ft. in diameter and 7¾ ft. in height. The interior part of the cylinder is divided into four chambers (L M N O), by means of three perforated disks (*b c d e f g*). K is the tube for conducting the carbonic acid from the furnace. At its entrance into the washing apparatus it is bent at right angles and closed at the end. The lower half of that part of the pipe which is in the washing apparatus is perforated by numerous holes, the diameter of which is at least equal to that of the tube. The carbonic acid enters through these orifices, then passes through the perforations of the three disks, and also through the layers of water upon the plates. The perforations of these plates are about ⅜ in. in diameter, and are arranged so that the whole surface occupied by them is equal to the diameter of the main pipe or a little more. The wash water enters through a small tube at *b*, and falls into a dish placed on the top disk where it overflows and covers the disk. Owing to the pressure of the gas, the water cannot pass through the perforations but remains over them until it reaches the height of the escape tube above, the gas all the while passing through it. The freshly admitted water falls through the outlet pipe into a similar dish upon the second disk, flowing over and covering this also; it then falls through a second outlet pipe on to the third disk, from whence it escapes into the lower chamber, where it collects until the openings of the main pipe are covered. The bent tube (H) now keeps the water at a constant level, and allows the superfluous water to escape. The water and the gas thus flow in opposite directions, and the gas which enters below is forced to make its way through the four layers of water. In no way can it make its escape, because the escape tubes are kept closed by the water flowing over from the dishes. The water meets the gas from above, and the arrangement is such that the same water is used four times. This is a systematic method of cooling and purifying at the least possible expenditure of material. Having reached the top, the gas is drawn off by the pump through the tube (O P) to a dry purifier, and afterwards conducted to the saturator.

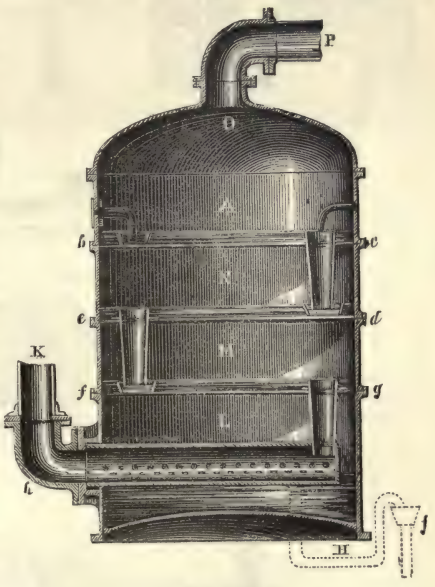


FIG. 613.

Fig. 614 represents in one view all the apparatus for the production and use of the gas. To the left hand is the lime furnace described. The limestone and coke are mixed in the given proportions upon the plate (*a*).

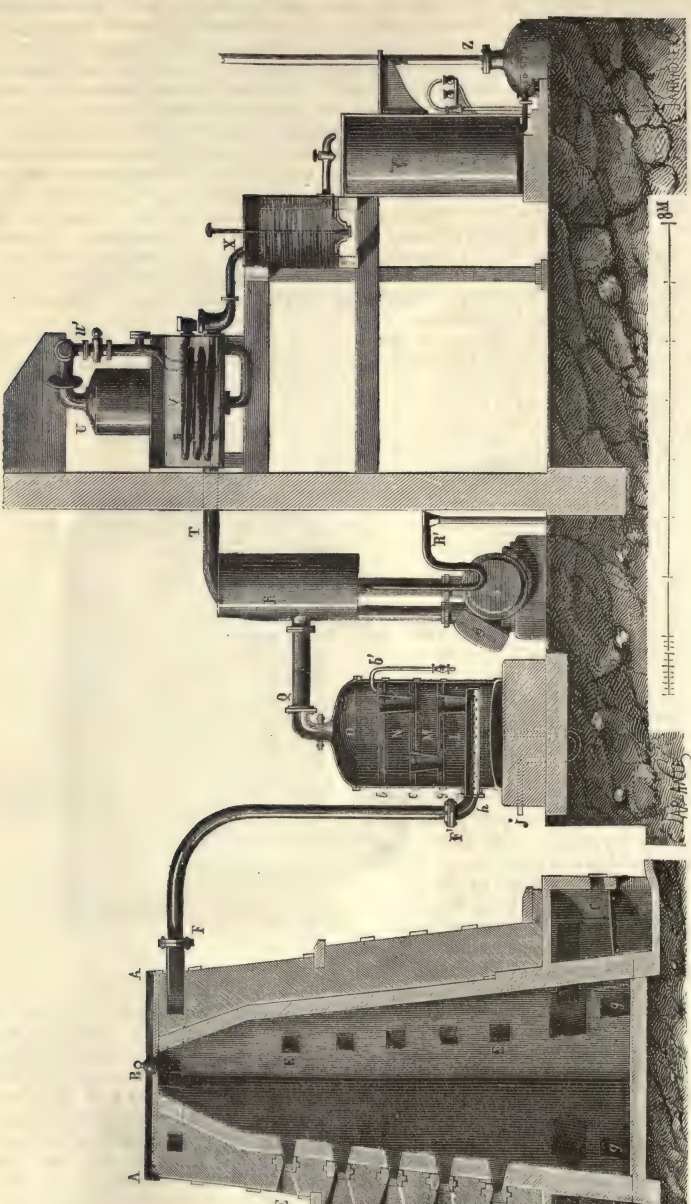


FIG. 614.

The hourly charging of the furnace is effected through the openings in the plate closed by the three balls (B). The burnt lime is withdrawn every hour through the

openings (*g g*) below. The carbonic acid rises to the top of the furnace through the spiral channel, and is then conducted to the first washing apparatus by the pipe F F′; it then rises through the apertures in the extension of this pipe (*h*), passes into the chambers (L M N O) through the perforations of the disks, and is washed by the water entering at *b′*. The washed gas then passes through the tube Q into a dry purifier (R), which is advantageously filled with coarse pieces of limestone, and here any water mechanically carried over with the gas is deposited and runs off through a bent tube (R′), S is a horizontal air-pump which draws the gas to this point and then forces it on through the tube (T) into the receptacle (U), where it is under a pressure of from 6½ to 10 ft. of water, causing it to flow into the saturator upon the opening of the cocks which govern it. V is one of the saturators, and X is the clarifying vessel in which the saturated juice deposits its precipitate. For the purpose of separating the clear liquid from the precipitate on the bottom there is a simple arrangement. To the escape cock upon the inside of the clarifying vessel, a wide caoutchouc tube is attached, upon the end of which is a float, keeping the open end constantly on a level with the liquor. When the turbidity is deposited the stopcock is opened, the clear liquid runs off through the tube into the receptacle (Y), and afterwards the precipitate is withdrawn through a valve at the bottom of the vessel, and is conveyed by a monte-jus (not represented in the cut) to the filtering presses. From the receptacle (Y), the clear juice either flows immediately into the charcoal filters, if the apparatus for saturation and clarification are above them, or if not, it is raised to the filters by a monte-jus.

Various other methods, having for their object the production of concentrated carbonic acid, however, are not practically available, because the extra expense of producing it is by no means proportionate to the advantage gained. It has been proposed, for instance, to heat lime in closed iron retorts by a stream of superheated steam. Another plan consists in passing carbonic acid from lime kilns into a solution of neutral sodium carbonate; the carbonic acid being absorbed and acid sodium carbonate formed, whilst the nitrogen of the air entering the furnace and the carbonic oxide gas produced pass off through the liquid. The solution of acid sodium carbonate is then heated to boiling, causing the evolution of the absorbed carbonic acid, neutral sodium carbonate remaining, which can be used in a fresh operation.

The first effect of the carbonic acid is to produce a cloudiness of the juice, due to the precipitation of calcium carbonate. After a short time the precipitate gathers in large flocks and settles to the bottom. The liquid is examined from time to time during the saturation, by removing a small portion with a little iron spoon. The progress of saturation is shown by the appearance of the liquid, an insufficiency of carbonic acid being indicated as long as it remains cloudy, but when large flakes appear and quickly settle to the bottom of the spoon, leaving the juice above clear, the saturation is complete.

The supply of carbonic acid is then stopped, the liquid is once more brought to ebullition, and then immediately drawn off into a clarifying vessel standing directly under the saturator, where in a very short time the precipitate subsides. The fluid is now filtered and the precipitate expressed together with the scum.

The precipitate formed in the process of saturation is not pure calcium carbonate, but is mixed with various nitrogenous and non-nitrogenous organic substances. Whether this further precipitation takes place because the substances in combination with the lime were dissolved in the juice previous to its saturation, and were then thrown out of solution, or whether they are mechanically carried down by the calcium carbonate, is not known.

The treatment with carbonic acid is never carried so far that all the lime is removed from the sap. A small quantity of it is always allowed to remain, because it has been observed that in the subsequent decolorisation by animal charcoal, a much more complete result is obtained if the juice still contains some lime; for although juice free from lime can be perfectly decolourised, it readily turns dark afterwards. It appears therefore that after the clarification, the juice contains a substance colourless in itself, but which undergoes change and becomes coloured, and that this substance in combination with lime is absorbed by charcoal, while it is not absorbed in a free condition.

Rousseau's Method of Clarification.—According to this method the juice is clarified in pans such as have been described, but six times the ordinary quantity of lime is used, or sufficient to combine with not only the non-saccharine matters—organic acids, etc.—but also with the whole of the sugar. On an average 4 lbs. of lime are used to 100 gallons of juice, varying according to the quality of the beets. The lime is mixed with 5 or 6 times its volume of hot water and added to the juice at a temperature of 60° to 65°. The mixture is then heated to 90° or 95°, but should not be made to boil. The liquor is separated from the precipitate and passed through a

small filter to remove suspended particles of lime scum. This filter consists of a box having a strainer at the bottom, over which a cloth is spread, and this is covered with a layer of granular animal charcoal 10 inches thick.

The clear juice is saturated in the apparatus represented in fig. 615. It consists of a double-action air pump (A) worked by machinery, by which air is drawn in through the pipes (*a a*) and driven through the pipes (*b b*) into an iron furnace (B), on the base of which is a mixture of charcoal and coke. When the carbonic acid produced by the combustion is not used it escapes through the valve (S). When this is closed, the combustion products go through the pipe (c c′) into the washing vessel (D), supplied with water, where suspended ash is deposited; the dirty water can be run off through the cock (*d*″). From the wash vessel the carbonic acid passes through a pipe (F), common to all the saturators, and the branch pipe (G H) into the saturator (I). The saturator has the same construction as the ordinary defecation pan. It is a boiler with an arched bottom, under which is a steam jacket; this is supplied with steam through one pipe (N), whilst another pipe (O) conducts the condensed water and excess of steam into a steam chest.

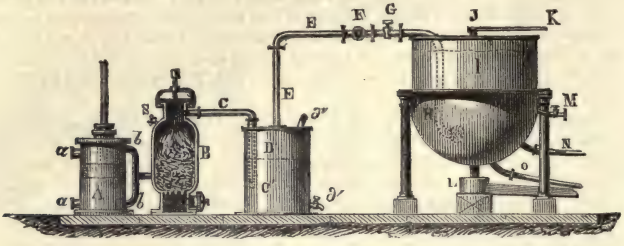


FIG. 615.

The vessel (I) is filled with clear juice, which is then heated to boiling and treated with carbonic acid. The gas enters through a rose at the end of the pipe (G H), by which means it is driven in separate bubbles through the liquid. The completion of the saturation is recognised by the liquid becoming less viscous, and allowing the precipitate of calcium carbonate formed to sink readily to the bottom. A valve at the bottom is then opened by turning the rod (J K), and the juice runs through the trough (L) into the settling vessel, or through a box filter into a reservoir, ready to be passed through the principal filter. It is evident that by this method a large quantity of scum is produced, and for this reason it has not met with favour in the German works. Recently special apparatus has been constructed facilitating the working of the scum, but at the same time the methods of defecation have been improved.

Perrier Possoz-Jelinek's Methods of Defecation.—The peculiarities of these methods are usually united in working. The cold juice is mixed with milk of lime heated and saturated; after the resulting defecation milk of lime is added a second time, and it is again saturated. The milk of lime used contains 20 per cent. of lime. It is made by mixing 480 lbs. of burnt lime with about 130 gallons of water or defecated juice, and afterwards diluting this paste with 650 gallons more liquor; the milk is passed through a coarse sieve to remove stones and sand. It will then contain nearly 20 per cent. of lime, but in order to bring it to its right strength 10 c. c. are removed with a pipette and diluted with 200 c. c. of water, in which 50 grams of pure sugar is dissolved, and thus all the lime is obtained in solution as sugar-lime. The solution is then coloured blue with litmus, and titrated with normal sulphuric acid. After the amount of lime has been thus ascertained, it is easy to reckon how much water has yet to be added to bring the solution to the right strength.

In the first treatment with lime, when the liquor is kept alkaline, the greater part of the foreign substances is separated. In the second treatment with lime, when a very much smaller proportion is used, the remaining impurities are got rid of. The saturation with carbonic acid is then carried so far that all the compounds of sugar with alkalies and lime are decomposed. At the same time the excess of carbonic acid causes a small portion of the impurity to pass into solution again, and in order to get rid of this a small quantity of lime is added, insufficient to produce any detrimental effect upon the subsequent boiling.

The clear juice is mixed with the milk of lime in such proportions that 15 to 30 parts of pure lime are added to each 1,000 parts of juice. Usually 20 parts are sufficient, but the quantity must be regulated by the quality of the beet. The mixture is

brought by means of a monte jus into the apparatus for defecation and saturation, vertical and horizontal sections of which are shown in figs. 616 and 617. It consists of a square cistern 6 feet 8 inches long and 4 feet deep. At the bottom lies a pipe (*a*) 4 inches in diameter, united by four kneepieces, and forming a square parallel to the walls of the cistern. This pipe is perforated over its entire surface with fine holes, in order to distribute through the liquid the carbonic acid, which is carried to it by a vertical pipe with a cock (*u*). A 3½-inch spirally bent steam pipe (*c*), the three coils of which are about 6 inches apart, obtains direct steam from the pipe (*b*); the condensed and uncondensed steam passing off through *f* into a steam chest. A 5-inch valve pipe (*d*) is used for emptying. When the cistern is full of the mixture of juice and lime, steam is let into the spiral, and carbonic acid is admitted at the same time. A layer of froth of considerable consistence immediately begins to form, for the dispersion of which an addition of fat is always requisite. A simple arrangement for the prevention of the froth has been introduced by Evrard. Two 2¼-in horizontal pipes are placed at a distance of 40 inches from each other, 6 inches below the edge and 20 inches from the sides of the box. Both pipes communicate with the steam, and on two sides they are perforated with fine holes. When steam is let in it is driven horizontally in a fine stream through these openings, makes its way through the frothy mass, and causes the bubbles to burst. By the aid of these froth breakers —émousseurs—the work can be carried on rapidly without fear of boiling over.

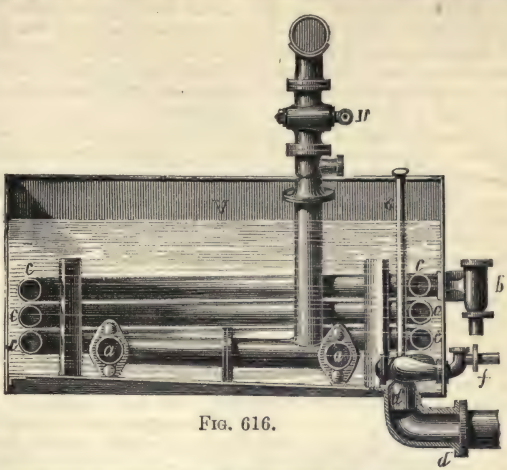


FIG. 616.

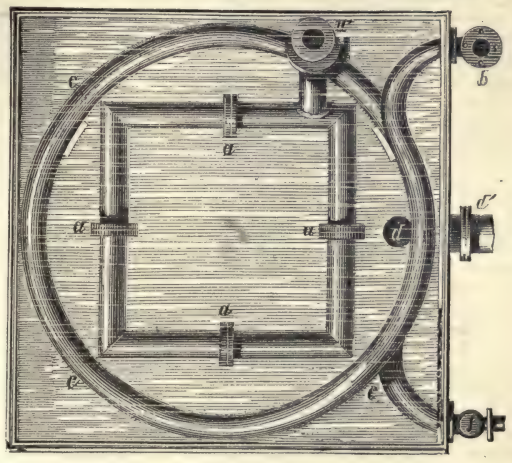


FIG. 617.

Under the continued inflow of the carbonic acid the temperature of the juice rises from 60° to 80°, and it is retained at this temperature until the precipitate sinks readily in great flocks to the bottom, and the liquor only contains 1 to 3 parts per 1,000 of dissolved lime; the temperature is then raised to 90° or 95°. The juice thus treated separates easily from the precipitate, which does not rise as in the ordinary defecation to the surface, but collects at the bottom. As soon as the defecation is completed, the valve at the bottom of the cistern is opened, and the juice and sediment run out into a clearing vessel. After a short time two-thirds of the juice can be separated clear from deposit; the remainder with the sediment is passed into the filter press, where the sediment is completely retained, and the juice is obtained clear.

The whole of the juice is then brought back to the saturator, when an amount of milk of lime corresponding to 5 lbs. of pure lime to each 100 gallons of juice is added

and the whole is boiled for five minutes. The steam is then shut off, and carbonic acid is let in until all lime and alkali is completely neutralised, turmeric paper not being coloured brown, or red litmus paper blue, by a few drops of the juice. Excess of carbonic acid, by which some of the precipitated impurities are redissolved, is then removed by boiling, and a slight alkalinity is restored to the liquid by the addition of ½ lb. to 1 lb. of lime to each 100 gallons. After settling, the clear juice goes to the filter, and is then boiled in the usual way.

The advantage of this method is that the cold beet juice dissolves a much larger quantity of lime than at a higher temperature, and consequently the precipitation of the matters forming insoluble compounds with lime can be more easily effected. The large excess of sugar lime is at once again decomposed through the saturation, calcium carbonate being precipitated, carrying down with it foreign matters. The resulting precipitate is dense and compact, and can be more easily freed from juice than the voluminous slime of the ordinary defecation.

Filtration of the Juice.—After the defecation of cane juice it is allowed to run through a small preliminary filter into the filter which has already been used for the filtration of thick juice (see p. 847). The filtered juice has a specific gravity of about 1·063 (17° sacch.); it is then concentrated to about sp. gr. 1·118 (30° sacch.) The juice flowing from thence is collected in a reservoir, from which it is drawn as required into the evaporating body of a vacuum apparatus (p. 849). The thick juice is then at once boiled to the thread proof or granulation.

The advantages of the improved arrangements in colonial sugar factories consist in an increased yield of 33 per cent. from the cane, and the product commands about 10 per cent. higher price than that prepared by the old method. The rapid evaporation in the vacuum pans allows of a larger quantity of cane being worked in the same factory. A large central factory can therefore be erected in the midst of several plantations, in which the cane produced in the different places can be worked, and a separation thus effected between the strictly agricultural and the manufacturing works. A large manufactory of this kind exists in Havanna; it unites the work of four old boiling houses—St. Thomas, St. Susanna, St. Martin, and Zuluetta—and produces 125 tons of sugar daily. Another central manufactory, erected by Cail and Souques, at Point-à Pitre, Guadeloupe, receives by water the cane harvest of the entire coast; a canal bears the ships to a railway that has its terminus at the manufactory. This central manufactory is erected for the working of 1,000 tons of cane daily, with a yield of 100 tons of sugar.

By the clarification and saturation, a great many non-saccharine constituents are removed from the juice; but others still remain, which would hinder the crystallisation of the sugar, especially in the case of beet juice. To remove these, animal charcoal is employed. Animal charcoal is obtained by heating bones to redness out of contact with the air, and has the property of attracting to its surface and rendering insoluble most diverse substances contained in solution. Its power of absorbing colouring matter has been long known; but it also absorbs various organic substances, such as salts of organic acids, calcium citrate, for example (which, according to the researches of Kunze and Reichardt, is completely withdrawn from solution by filtration through animal charcoal), calcium succinate, and others. Inorganic substances are also removed, such as salts of the alkalies and alkaline earths, calcium sulphate, free alkalies, and caustic lime; in fact, animal charcoal effects transformations of the most diverse kinds. According to Kunze and Reichardt, upon filtering solutions of calcium chloride through animal charcoal, 26 per cent. of the dissolved salt is absorbed; and from a solution of sodium citrate 35 per cent. But if a solution containing both calcium chloride and sodium citrate is similarly filtered, 98 per cent. of the citric acid, 65 per cent. of lime, 8 per cent. of the chlorine, and 3·4 per cent. of the soda, are absorbed, so that evidently the animal charcoal decomposes the sodium citrate and calcium chloride into calcium citrate and sodium chloride, the first of which is readily absorbed, and the second only in small quantities. The absorbing power of animal charcoal for lime is so great, that before the process of saturation was known the whole of the lime was removed from the juice by this means. Of course, as the absorbing capacity of the charcoal is limited, a very great quantity was requisite, and hence it is a great gain to the manufacturer that this part of the work can now be effected in an easier and less expensive manner. Under all conditions the amount of non-saccharine matters is always considerably reduced, and the proportion of sugar is improved, by the use of animal charcoal.

The condition of the charcoal has a great influence upon the filtration. As it absorbs by surface attraction, that charcoal will be the most effective which has the greatest surface, and contains most pores. The best charcoal is prepared from hard bones, and is of a dull black colour. Brown charcoal which is not burned sufficiently is worthless, and may even spoil the juice. A shining black sort of animal charcoal is

equally unserviceable, not being porous enough, its pores being closed with layers of dense charcoal.

Formerly, animal charcoal was used in the form of a fine powder. But as this is only separated from the juice with difficulty and loss, it is now universally used in pieces about the size of a bean. The juice passes easily through such pieces of bone black, and becomes in the process quite pure and clear, whilst the charcoal remains in the filtering apparatus.

The filters of modern construction are always completely closed. A considerable number of them are always placed alongside of each other, and are united by means of tubes in such a way that they are capable of being worked separately or together, the sap passing through the first filter and afterwards through the others. Filters united in this way are called a filtering battery.

One of the filters belonging to a battery is shown in fig. 618. It consists of an iron cylinder (A), closed above and below, 2 feet in diameter, 10 to 16 feet high. Close to the bottom is a perforated iron plate (B), covered with a cloth. Upon this the charcoal is thrown in such quantities that the cylinder is almost entirely filled. The manhole (H) serves for admitting the charcoal, and a second manhole (F) is used for removing the charcoal that has become exhausted. Both are tightly closed while the work of filtration is going on, by means of screws. The liquid to be filtered is admitted through a perpendicular pipe (E), which is in connection with four other pipes fixed in a horizontal position (I J K L), that run the whole length of the battery. One of these pipes is shown on a larger scale by fig. 619. If, for instance, the first filter be in action, the object being to filter juice from the pipe (I), the cocks (J K L) are closed, and the liquid will then pass through (I) into the perpendicular pipe (E), and flow into the filter. If the second filter is to be filled with the juice from L, in this case the cocks I J K will be closed, and L left open. The juice being admitted from above, passes through the layer of charcoal, and appears again below; there it enters the pipe (C D), bent upwards perpendicularly, and is conducted by it to one of four channels (*m n o p*), which it enters through a funnel, and is carried off. By means of the cock at (E), the juice is completely removed from the cylinder.

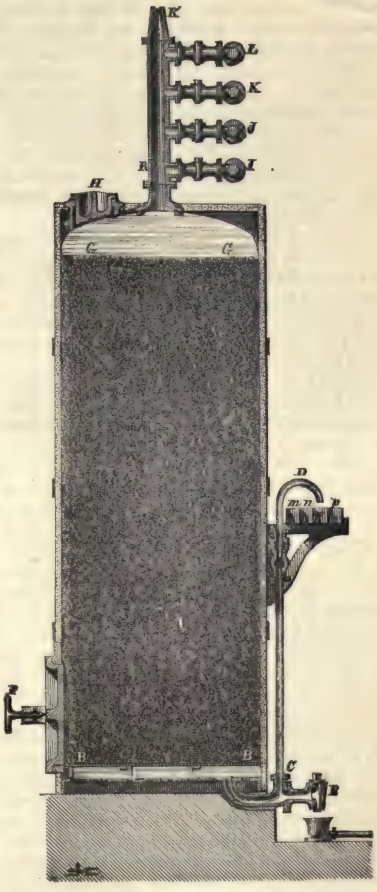


FIG. 618.

If two filters are to work together, another arrangement is requisite which is now in general use. The vertical tube (C D) in such case extends above the head of the filter, where it forks into two tubes, each of which is shut by a cock. One of these allows the juice to escape immediately into the channels, which are now placed somewhat higher than before, and the other inclines upward and opens into the perpendicular pipe of the next filter, uniting thus the first and the second. In a similar way the second may be united with the third, this with the fourth, and the last joined again to the first. If juice be admitted into the first filter, the cock of its escape pipe being closed, and the pipe opened which connects the first filter with the second, the

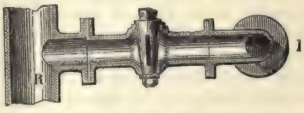


FIG. 619.

juice must necessarily, after it has passed through the first, go on to the second, and be then filtered a second time. Thus, the same juice could be passed successively into all the filters, but two filters worked together are sufficient. In filling the filter, the perforated bottom, covered with linen cloth, is put in its proper position through the opening (F), and a layer of coarse charcoal is spread evenly over it. The lower manhole is then closed, and the cylinder filled about half full of water by opening the cock (L). The object of the water is, that the charcoal introduced at the upper manhole may be disposed in regular and uniform layers. The cylinder is then filled up to the point G with charcoal, when the manhole (H) is closed, an air cock situated at the top of the vertical pipe (K′) is opened, and the water is allowed to flow away by opening the cock (B). The air cock is then closed, and the steam cock (K) is opened. The water is thus driven off and the whole filter warmed. Steam is allowed to enter until it ceases to condense, and escapes in large quantities at E. E and K are now closed and J opened. This admits the thick juice which at once drives out the water remaining in the pores of the charcoal through the pipe D; after which the pure juice itself flows away.

If the filter has just been filled with the charcoal, the first juice which escapes is sufficiently pure, and is conducted through D at once into the channel intended for it. After a time the juice is no longer sufficiently pure and colourless. The escape is then cut off and the juice is carried to a second filter, which has in the meantime been freshly filled.

When juice of the requisite purity is no longer yielded by this second filter, the first filter is not used for the thick juice. The cock at J is now closed, and the one at I opened, through which thin sap is admitted. This is first allowed only to flow through the first filter, while the second still receives thick juice for a while through its perpendicular pipe. If the thin juice is not rendered colourless by one filtration, then the thick juice is shut off from the second filter, and the thin juice is passed over from the first into the second.

In this way the absorbing power of the charcoal is exhausted as much as possible. The thick juice being much purer than the thin, gives up comparatively little to the charcoal, which therefore does not become greatly saturated with impurity, and is still able to remove a considerable quantity from the thin juice.

When the charcoal becomes so greatly vitiated by the thin juice that it is no longer effective, the water cock is opened and water is permitted to flow in until all the thin juice still remaining with the charcoal is driven over through the connecting pipe into the second cylinder. The water is then run off through the cock (B), the charcoal is removed through the manhole (F) and the filter freshly filled.

During the filtration the filter is kept constantly filled with the juice, which is effected by regulating the height of the escape pipe (C D). Care is also taken to keep the juice as hot as possible while in the filter, as the action of the charcoal is greatly promoted by heat. A current of steam is therefore directed through the filter immediately after it has been filled with fresh charcoal, whilst the juice is brought hot to the filter without any delay after the process of clarification by saturation. To prevent cooling during the filtration, the cylinder is placed in a warm situation, and sometimes is surrounded by bad conductors of heat.

Revivification of the Animal Charcoal.—The animal charcoal, after becoming clogged up, is not worthless, but can be used again and again after the absorbed substances have been removed from it. This process of removing the absorbed substances is called revivification. The animal charcoal is taken from the cylinder and thrown into large vats, where it is flooded with water, to which a small quantity of hydrochloric acid has been added. The hydrochloric acid dissolves the lime which has been absorbed; but an excess of acid must be avoided, since this would dissolve the calcium phosphate to which the charcoal owes its density, and the charcoal would be injured. An active fermentation commences which destroys the organic substances and renders others soluble. When the fermentation ceases the water is run off, and the charcoal washed with fresh water. It is then dried and heated to redness, when it is again ready for use.

Evaporation of the Juice.—The juice as it flows from the filter is not more concentrated than when it comes from the crusher; for although in the processes of clarification and saturation it is heated, yet the amount of concentration is not worth mentioning, because in the lime clarification, at least as much water is added as is removed by evaporation, and the further evaporation during the process of saturation is counterbalanced by the water used in washing and cleaning the filter. It may be assumed that the juice when ready for evaporation marks on an average 7° or 8° on the scale of the saccharometer, and that the liquor has to be reduced by evaporation to one-fifteenth or one-sixteenth of its volume to effect the crystallisation of the sugar.

The evaporation consists of two operations. In the first the thin juice is brought

to a specific gravity of about 1·490. This process yields thick juice, and may be designated the evaporation. The thick juice is subjected to another operation called boiling, by which it is brought to the point of crystallisation.

The evaporation may be performed by—

(1.) Heating directly over a fire.

(2.) Heating by means of steam.

(3.) Heating by means of steam in a partial vacuum.

The first method may be regarded as obsolete, as it is not now employed in good sugar factories. The disadvantages are the following: the juice is exposed to injurious changes; it requires the utmost attention to prevent the juice from burning, and lastly the constant action of the air causes a coloration of the juice.

To avoid these disadvantages, heating by steam has taken the place of heating directly by fire. The apparatus used is various. Pecqueur's apparatus (fig. 620) consists of an evaporation pan (A), made of sheet copper, and having the form of a long horseshoe. The bottom is flat and the sides are vertical. It is supported by iron feet (D E). At one end are pivots which can be turned upon two beds in the foot (E), and a pressure upon the bar (B) is sufficient to give an inclined position to the whole pan, as is indicated by the dotted lines. The object of this turning arrangement is that the pan may be more easily emptied. When the process of evaporation is finished, the juice is run off through the cock (C), which takes place readily with the pan in a level condition when it contains a quantity of juice, but for the purpose of removing the bottom portion the inclined position is given. Heat is applied by means of six tubes in the shape of a horseshoe, all united together (fig. 621). These six tubes lie in a horizontal plane, and their ends are fastened to two supporting pipes which do not directly communicate with each other. The steam is admitted at R directly into one of the supporting pipes, and passes through the whole length of the six tubes, and into the second supporter, from which it escapes into a collector, the object of which is to remove the condensed water as well as sustain the tension of the steam. The ends of the pipe supporter (R) pass through the pivots upon which the apparatus is turned, and these pivots thus serve as stuffing boxes for the pipe supporters. The heating tubes can be easily removed from the floor of the pan and every part of them reached, so that they can be frequently washed. This is a very necessary operation, as in the process of evaporation of the thin sap a part of the impurity contained in it—lime salts, for example—is deposited upon the bottom of the pan and on the surface of the tubes, forming a layer which hinders the passage of the heat and impairs the process of evaporation. To clean the apparatus, very dilute hydrochloric acid is poured upon the bottom until this, as well as the coating upon the tubes, is covered. After the acid has acted a short time, it is run off. The tubes are then raised into a perpendicular position and all dirt removed with brushes, etc.

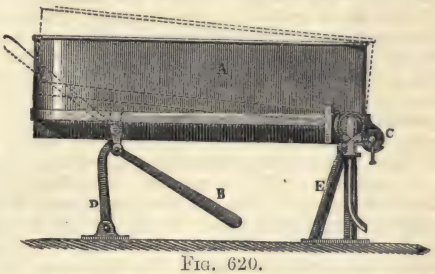


Fig. 620.

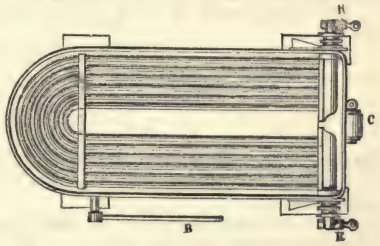


Fig. 621.

The rapidity with which the evaporation of the juice goes on depends upon the difference between its boiling point and the temperature of the heating surface. Therefore steam of very high tension is used (about five atmospheres), which brings the temperature of the tubes up to 152° C. This great heat is of no disadvantage because the juice cannot be heated above its boiling point as long as it surrounds the steam pipes on all sides. The pan must therefore be kept filled during the process of evaporation, or at any rate, the level of the liquid must not be allowed to sink so that any part of the pipes is left uncovered, for in such case the juice at that point would be burned.

Steam of a tension of 5 atmospheres effects the evaporation of about 120 lbs. of water per hour from every 10 square feet of heating surface.

Another very suitable apparatus for the evaporation of juice is that which was introduced by Claes de Lembeck of Brussels. It consists essentially of a some-

what coined cylinder about 16 feet in height. The jacket is filled with steam under a pressure of 4 or 5 atmospheres. The whole surface of the cylinder inside as well as out is kept constantly covered with a thin layer of the juice to be evaporated. The juice is supplied from a reservoir above, and as it flows over the heated surfaces of the cylinder it is rapidly evaporated.

The danger of overheating the juice is even greater with this apparatus than with Pecqueur's pan, and consequently it is little used.

A third method of effecting the evaporation by steam heat is to connect the vessel in which the thick juice is boiled with a serpentine pipe communicating at the other end with an air pump, and in this way to boil down the thick juice under reduced barometric pressure, at the same time making the thin juice flow over the surface of the serpentine pipe, heated by the steam given off by the thick juice.

It is evident that such a method of evaporation must be very imperfect. The quantity of the thick juice boiled down bears no sort of relation to the thin juice to be evaporated by the steam it furnishes. Further, in consequence of the rarefaction, this steam enters the heating pipes at a temperature much below the boiling point of the juice. The arrangement may serve the purpose of condensing the steam, but can never effect the required concentration of the juice, which must be completed in a boiling apparatus specially designed for this purpose. This apparatus may be profitably employed for the purpose of warming the juice, or for economising the water used in condensation in places where fuel is expensive or where water is scarce, as, for example, in the sugar cane plantations. But in the manufacture of beet sugar it is never used. This apparatus has the further disadvantage, in common with the Lembeck apparatus, that the juice is exposed to the air in thin layers, and is thus acted upon by the air, which always damages it by producing colour.

In all the better factories these forms of apparatus have been abandoned and the juice is evaporated *in vacuo*. The apparatus for this purpose was first introduced in the manufacture of sugar in America by Rillieux. It was then brought into the German factories at Magdeburg by Tischbein. It was afterwards essentially improved by Robert of Selowitz. Many changes in the apparatus have since taken place, but these affect only the details. The general principles upon which its construction rests have not been changed.

The arrangement of the apparatus depends essentially upon the following principles:—

The evaporation of water from a liquid is rapid in proportion to the difference between the boiling point of the liquid and the temperature of the heating surface.

Steam of a low temperature may cause rapid evaporation of a liquid if the boiling point of the liquid is below the temperature of the steam.

The boiling point of any liquid depends upon the pressure to which it is subjected. By diminishing the pressure, the boiling point of a liquid may be lowered.

The steam from any liquid has the same temperature as the liquid in which it was generated.

By increasing the heating surface the same result may be obtained with steam of a low temperature as with steam of a high temperature and less heating surface.

If, for instance, in a Pecqueur's pan there were, instead of six, as many as eighteen to twenty-four pipes of the same size, it would not be necessary to use steam at 150° to evaporate the amount of water indicated; the same result would be obtained by the use of steam of a much lower temperature. Instead of steam with a pressure of five atmospheres, the work might be done by steam under a pressure of one and a half atmospheres at a temperature of 112°. Such steam is constantly at disposal in great quantities in a sugar factory. The steam that has already been used for driving the machinery, instead of being allowed to escape into the air, can be led into a steam collector without materially interfering with the steam engine. The steam, too, which escapes from the jacket of the clarifying pan, and that which has been used to heat the liquid in the saturation vat, may also be led into a common collector, and after having been used for their special work, can still be used for the purpose of evaporating thin juice contained in an apparatus having a large heating surface.

Again, if the pan of Pecqueur were transformed into a large closed vessel, and the steam generated in it, which would have the temperature of the boiling juice, or about 100°, were to be conducted into the extended pipe system of a second Pecqueur pan, also closed, and from which air and steam were exhausted by an air pump and a condensing arrangement, such a diminution of pressure could be attained that the juice in this pan would boil at 85°. There would thus be a difference of 15° between the boiling point and the temperature of the heating surface, which would be quite sufficient to effect active evaporation.

Further, this second pan might in the same way be connected with a third, in which the boiling point of the juice through exhaustion of the air could be reduced to

70°. The steam formed in the second pan could then be used for the evaporation of the juice in the third pan.

Instead of the shape of the Pecqueur's pan, Rillieux adopted the form of the tubular boiler, conducting the waste steam from the manufactory through the tubes, and filling the boiler with the juice to be evaporated. The steam thus generated was led into the heating pipes of the second vessel, and from those into the pipes of the third vessel; after passing this it was completely condensed by contact with cold water. At the same time the second and third vessels were partially exhausted by an air pump. Robert's modification consists in the pipes not being used for the reception of the steam, but for the fluid to be evaporated, the space between the pipes being filled with steam. Robert also abandoned the horizontal position of the pipes, and placed them in a vertical position. This arrangement of Robert's has many advantages, although after all these alterations there is a tendency to return to the original machinery introduced by Rillieux and Tischbein.

In practice it has been found that there is some difficulty in carrying on the work with three vessels. Generally, therefore, only two are united together, or the three vessels are so arranged that either of them can, at will, be shut off from the others. In case there is an insufficiency of waste steam, arrangements are introduced to make use of direct steam.

The three evaporation vessels are technically known as the three bodies of the apparatus.

The evaporation in each of the bodies is regulated by bringing the juice in the first body to 20° of the saccharometer, in the second to 30°, and in the third to 50°.

In 1000 parts of thin juice at 8° there will be 80 parts of solid constituents, sugar, etc., and 920 of water. This is evaporated to 20° in the first body, and then contains 80 parts of sugar and only 320 parts of water; so that in the first body $920 - 320 = 600$ parts of water are evaporated. This juice of 20° is evaporated in the second body to 30° and then contains 80 parts of sugar, etc., and 187 parts of water; consequently in the second body $320 - 187 = 133$ parts of water are evaporated by means of the 600 parts of steam from the first body. Lastly, in the third body the juice is brought to 50°, and then contains 80 parts of sugar and 80 parts of water; so that in order to attain this degree of concentration $187 - 80 = 107$ parts of water are evaporated by means of the steam from the second body.

Consequently, in the first body, 600 parts of water are evaporated.
„ second „ 133 „ „ „ „
„ third „ 107 „ „ „ „

In all 840 parts of water.

There remain 160 parts of thick juice of 50° to be subjected to further processes.

The progress of the evaporation is ascertained by removing a small portion of the boiling liquid as a test, either by means of a gauge, after shutting off the communication between it and the inner space, or by means of a small apparatus, consisting of a glass tube connected with the vacuum chamber and fitted with cocks, so that a quantity of the juice can be drawn out as required, without disarranging the action of the pan.

During the evaporation, the non-saccharine constituents which were not removed by the first filtration are concentrated in the juice. A portion of them is precipitated in an insoluble form, in the body, covering the boiling tubes and the surface of the juice chambers with an incrustation of calcium compounds, especially calcium oxalate and lime soaps, the latter being formed by the action of dissolved lime upon the fat added. In course of time these incrustations impede the evaporation, as the heat from the steam no longer passes so readily through the walls of the tubes. Hence, from time to time, a thorough cleaning of the apparatus is necessary. For this purpose all the bodies are filled with water to which some hydrochloric acid has been added for the purpose of dissolving the lime salts; this is allowed to remain some time, the manholes being open. Lastly, the acidulated water is run off below, the apparatus steamed out, and after every tube has been scoured out with suitable cylindrical brushes, the apparatus is again rinsed out with water. As the hydrochloric acid employed, as well as the acids liberated from the lime salts, attack the iron, the apparatus should not be subjected to the action of acid longer than is absolutely necessary. Further, through the action of the acids upon the iron, hydrogen is liberated, which, mixing with the air, forms a very explosive compound. Hence, the apparatus should be allowed to stand for some time after the acidulated water has been removed, or what is still better, it should be thoroughly steamed out before approaching it with a naked light. Otto records an instance of a great disaster which occurred in a factory from neglect of this precaution.

In order to remove the impurities still remaining in the thick juice, it is again filtered through animal charcoal. It has already been mentioned that the freshly filled filters are always used at first for the thick juice. This is done as long as the filter has sufficient power of decolorisation. The filtered thick juice should be quite clear, and almost colourless.

Boiling down the Thick Juice.—In the operations previously described, the object has been, besides the concentration of the juice, the removal of foreign elements by the action of lime, carbonic acid, and animal charcoal, and consequently to attain a better proportion of sugar to non-saccharine matters. It is not possible to improve this proportion any further, and the next step is to obtain the sugar dissolved in the juice, which after the second filtration is designated technically clear liquor, in the solid form. It is therefore brought to crystallisation, so that the crystallisable sugar may be separated from the non-crystallisable or difficultly crystallisable bodies which remain in the mother liquor or treacle.

The following points are of importance to be noted:—

1. Cane sugar requires for its solution a certain amount of water.

2. A solution which contains sugar and water in such proportions that it will dissolve no more sugar is called a saturated solution.

3. A dilute solution is converted into a saturated solution by evaporation.

4. A saturated solution, if further concentrated, must deposit sugar, and this deposition takes place in the crystalline form as long as any solution remains.

5. A solution which is saturated at a low temperature will still dissolve sugar if the temperature be raised.

6. A boiling saturated solution upon a lowering of the temperature deposits a corresponding portion of its sugar, the result being a saturated solution corresponding to the temperature. If water be removed from this by evaporation, it yields when cooling a second crystallisation of sugar, and the mother liquor will yield upon further concentration a third crystallisation.

7. A saturated solution of sugar is still capable of dissolving other non-saccharine substances.

8. A boiling saturated solution containing non-saccharine matters will yield upon cooling almost pure crystals of sugar, while the non-saccharine bodies in the mother liquor and syrup become concentrated.

9. The non-saccharine matters impede the crystallisation of sugar.

10. When the amount of non-saccharine matter in a solution exceeds a certain quantity, such a liquid, although rich in sugar, will no longer crystallise, even if very greatly concentrated.

11. Saturated solutions of sugar boil under ordinary atmospheric pressure, at 115°–120°; under reduced pressure, the boiling point may be reduced to 50°–60°.

12. Concentrated solutions of sugar undergo change during protracted boiling in contact with air. They assume a colour varying from yellow to dark brown, part of the sugar being decomposed, and rendered uncrystallisable. If the boiling take place at a temperature of 50°–60° these changes do not occur.

The method of boiling the thick juice or clear liquor is essentially as follows: The juice on coming from the filter is evaporated *in vacuo* at the lowest possible temperature. The operation is carried on as rapidly as possible, until such a degree of concentration is reached that crystals form upon cooling (clear boiling), or while the liquid is hot (boiling to granulation). The crystals obtained in either way are removed from the mother liquor or syrup, and freed as completely as possible from adhering syrup. This crystallisation is called the first product. The syrup from this is further concentrated by clear boiling, and yields a second crop of crystals upon cooling. This second product is never so pure as the first; it is more coloured, and contains more foreign constituents; but the proportion of sugar to other substances is always more favourable than in the thick juice before the first crystallisation. The syrup from the second product upon being further evaporated yields a crystallisation of the third product. From the syrup of this third product a fourth crystallisation may be obtained if the beets have been of a good quality, and the juice has been well clarified in the different processes; otherwise the syrup will no longer yield crystals, and is now called molasses.

The first product is always a marketable article. The following crystallisations together with the after product go to the refinery, where each is subjected to further processes according to its quality.

If the second product is uncoloured and the crystals are well formed, the grain being sharp, it is often mixed with the first product. If the quality, however, is inferior, it would find a somewhat lower price in the market, as would also the subsequent products. In many cases, however, it is more profitable to convert the after

products into first product, and leave only a small quantity of after product. In the second product, as before mentioned, the proportion of sugar to non-saccharine matters is always better than in the thick juice. By the separation of the syrup from the after products, which can be easily effected with the improved machinery of the factories, a similar proportion between the sugar and non-saccharine matters is attained in them. Thus, if such after products be dissolved in the thick juice, not only is its quality not impaired, but it is even improved, because the relation of the constituents of the thick juice is improved, and more of the first product can be obtained from a similar amount of the thick juice, and almost all the after products can be converted into the more valuable article.

This operation is called the incorporation. In carrying it out the juice is not evaporated to the degree of concentration given above, but is removed earlier. Enough after product is then dissolved in the juice to make the solution indicate 50° on the saccharometer, and it is then subjected to the second filtration. The charcoal by this method removes non-saccharine matters not only from the juice, but also from the added after products, and the effect is a more complete clarification.

The boiling apparatus used in the operation is essentially the same as the last body of the Rillieux apparatus for evaporation; but as the amount of the clear liquor to be reduced by boiling is always much less than that of the thin juice, the apparatus is not so large, and instead of being cylindrical, it is either round, or the upper part is spherical and the lower part flat.

Howard's evaporating pan, as represented by fig. 622, consists of a copper pan (B B), fitted with a jacket (A A) and a dome (C C). Internally is fitted a coil of pipes (D D D) through which steam can be passed, entering through the valve (F), traversing the copper coil (D), and filling the steam jacket. To the top of the dome is fitted a

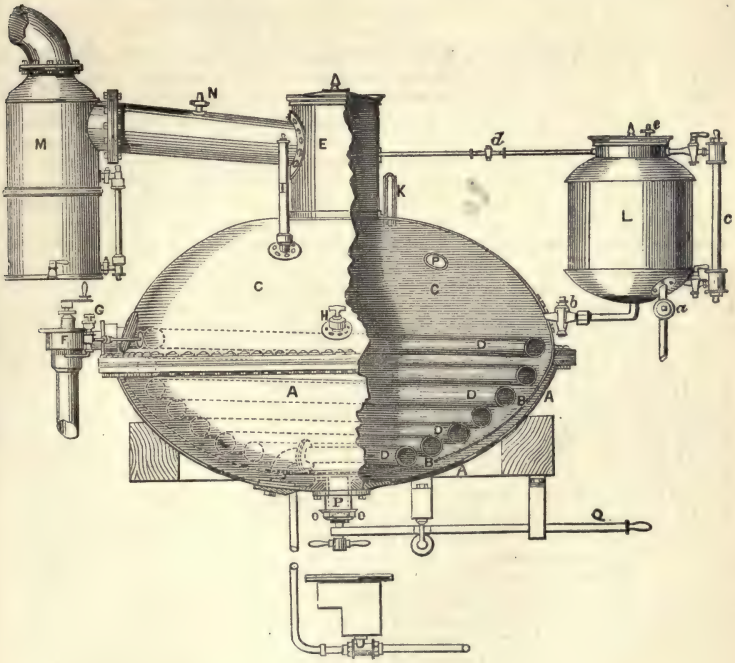


FIG. 622.

cylindrical steam chest (E), connected by means of a pipe (N) with the receiver (M), in which any particles of the juice carried over by the steam are collected. The vapour given off is condensed by jets of cold water, and by means of a powerful air pump a reduced barometric pressure is maintained within the pan during the whole operation. The liquor to be evaporated is supplied from the measure cistern (L), through the tap (*b*). In the dome of the pan are fitted a thermometer (I), a vacuum gauge (K), and an

apparatus called a **proof stick** (H), by means of which a sample of the contents may be removed without allowing air to enter. When the operation is completed, the contents of the pan are let out through the discharge cock (F).

A modified construction of the vacuum pan is represented by figs. 623 and 624. The form here used is that of a short vertical cylinder, the bottom as well as the top



FIG. 623.

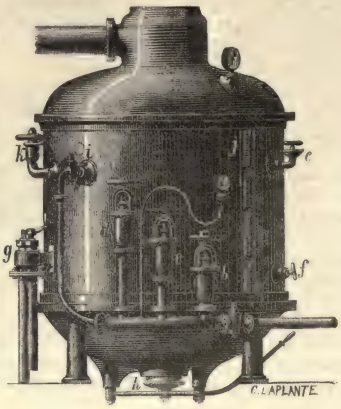


FIG. 624.

being arched. The heating is not effected by means of a jacket, but through three spiral pipes inside the vessel, each coil being connected at one end with the steam boiler and at the other end with a vessel into which the condensed steam runs off.

The operation of boiling differs somewhat according as the juice is to be merely concentrated or boiled to granulation. The first method, boiling blank, is practicable with all kinds of juice without exception, the second only with very pure juice.

For the blank boiling the valve in connection with the juice reservoir is opened, and the air pump being set in operation the juice is drawn in; when the apparatus is two-thirds full the valve is closed. The condition of the liquid can always be observed through glasses fixed to the side. Steam being introduced, and the flow of water to the condenser and the action of the air pump increased, the juice soon begins to boil and evaporates very rapidly. From time to time fresh juice is introduced in order to keep the apparatus as full as possible, so that at last, notwithstanding the diminution of volume caused by evaporation, the entire apparatus becomes filled with finished juice. The juice being now too thick to permit the use of the saccharometer, to ascertain the finish of the boiling, what is called the **thread** or **string test** is used. This is done by trying a drop of the juice between the thumb and fingers; the correct consistency is reached when the liquor is so viscous that it forms a thread, which breaks upon the separation of the thumb and finger to a certain distance; if insufficiently concentrated no thread is formed; if too much so, the thread stretches to a longer distance.

For taking out some of the juice to test the apparatus cannot be opened, as this would destroy the vacuum, neither can it be obtained through a tap, which would admit air but would not give passage to any juice. A special implement, called the **proof stick**, is therefore used. It consists of a bronze tube, running obliquely downwards, so that the lower end reaches almost the middle of the boiling space, whilst the other end opens on the upper side of the pan. The tube is closed at its lower end, but has in its side a circular opening ½ in. in diameter. Within the tube is a capsule that can be rotated, which is closed below, open above, and has in its side a similar circular opening. When the capsule is turned so that its opening corresponds with that of the tube it is in communication with the interior of the apparatus; in any other position all communication is cut off, so that air cannot penetrate in this way. In order to take a proof, a solid piston having a cavity corresponding with openings in the tube and capsule is thrust into the capsule and turned, so that its cavity and the openings in the capsule and tube are in accord; a small quantity of juice flows into the cavity, the piston and capsule are turned so as to shut off the communication, and the piston is withdrawn containing the juice for testing. As soon as the string test shows the boiling to be finished, the action of the air pump and condenser is stopped, air is admitted by opening the air cock, the steam is shut off, the finished

syrup is then run off through the out-flow valve, and the apparatus is ready for a fresh operation.

During the boiling of the juice certain contingencies may arise that exert an injurious influence on the operation. With inferior or imperfectly clarified juice it may happen that it does not boil regularly, but froths strongly and threatens continually to boil over. Loss can then be prevented only by very careful regulation of the temperature, not admitting too much steam, and boiling more slowly under rather more pressure. A sudden ebullition can be rendered harmless by some fat, as the steam bubbles burst more rapidly under a layer of fat; also by the admission of air through careful momentary opening of the air cock.

The reverse happens when the juice contains an excess of lime or other alkali. The alkali can only be in the juice in combination with the sugar, and these alkaline sugar compounds have the property at a certain point of the concentration of the juice to arrest the boiling and the rapid evaporation, and at the same time to decompose a portion of the sugar with the formation of coloured products. It is not known how the alkaline sugar compounds so influence the boiling. Under such conditions the boiling cannot be carried successfully to a termination, and nothing remains but to remove the syrup from the apparatus, dilute it to the consistence of thick juice, and filter it afresh.

In most cases the lime and alkali are removed in sufficient quantity by the action of fresh charcoal; but if simple filtration be insufficient, dilute sulphuric acid is added, which sets free the sugar and combines with the lime and alkali to form salts that do not interfere with the boiling. This neutralisation with acid must, however, be effected cautiously, and the greatest care taken to avoid any excess, since the smallest quantity of free acid would, upon heating, make the whole of the sugar uncrystallisable. Only so much acid must be added as to leave the juice still with a faintly alkaline reaction sufficient to colour turmeric paper brown or red litmus paper blue. With such juices as are known by experience to boil badly, the neutralisation of the alkali is regularly effected previous to the last filtration. Phosphoric acid, instead of sulphuric, is chiefly used for this purpose, as it forms with the lime an insoluble salt, which can be separated in a small preliminary filter.

In the blank boiling, the finished juice becomes a saturated solution at the temperature at which the boiling is carried out; the deposit of the sugar in crystals only takes place upon cooling. In the boiling to granulation the concentration is carried much further, and a syrup is obtained in the vacuum, that no longer holds in solution all the sugar it contains even at the boiling point, but in which a large portion of the sugar already exists as crystals. By boiling to granulation, therefore, there is finally obtained after the cooling much finished product and little syrup; whilst by blank boiling, the quantity of syrup is much more considerable. By boiling an impure juice to granulation, a crystallisation would be obtained, so enclosed in the mother liquor or syrup containing the impurities that it could not be perfectly separated.

In a manufactory daily working up 250 tons of beets, two vacuum pans of the form shown in figs. 623 and 624 are used. They are 7 ft. 8 in. in diameter, 8¼ ft. from top to bottom, and hold each upwards of 1,300 gallons of juice.

In boiling to granulation the air is first driven out from the boiling space by a jet of steam; the condenser and air pump are then brought into action, and the clarified juice is drawn into the pan, the height being observed through four glasses in the side. When the juice reaches the level of the lowest glass the juice valve is closed, and steam is admitted by the opening of the cock (*b*) into the lower spiral. By means of the condenser and the air pump a rarefaction is attained corresponding to 4 or 4·5 inches on the barometer; the pressure of steam in the spiral reaches five atmospheres, corresponding to a temperature of about 150°. Under the reduced pressure the juice boils at 60°; there is, therefore, a very considerable difference between the temperature of the heating surface and the boiling point, and the evaporation goes on rapidly. Juice is continually introduced in such quantity as to maintain the surface of the liquor nearly constant, until a concentration of about 70° to 72° of the saccharometer is obtained. The evaporation is then somewhat slackened by allowing the pressure in the interior to reach 10 inches of the barometer, and reducing the steam pressure in the spiral to two atmospheres, or 122°. Small quantities of fresh juice are successively drawn in so that the concentration is kept near the above point. As the surface of the liquor rises, the two other spirals are successively brought into operation. When the liquor covers the topmost observation glass, the juice valve is closed, and the whole is boiled to strong proof. When this point is reached, the temperature of the syrup is reduced to 50°–55°, with an atmospheric pressure of 2 to 3 inches, the steam in the spirals being under a pressure of two atmospheres, or about 122°. At this lower temperature a formation of sugar crystals

commences immediately, which can be recognised by the pasty appearance of the mass as seen through the glasses. As the evaporation proceeds small quantities of juice are admitted, until at last the whole apparatus is full of a pasty mass of sugar throughout which numberless crystals are distributed.

After seven or eight hours the boiling is completed, the air pump is disconnected, the air cock is opened, and the syrup is allowed to run off through a valve at the bottom and a trough into the crystallisation vessel, which must be sufficiently spacious to receive the entire product of an operation, or above 8½ tons.

Seyfert proposes to improve the syrup during the boiling, by adding to it an aqueous solution of sulphurous acid, which bleaches a portion of the colouring matters and also decomposes the compounds of sugar with lime and alkali. The sugar crystals thus obtained are very light coloured, well crystallised, and free from foreign taste or smell. It appears, however, that sugar so treated is not so easily refined as that to which no sulphurous acid has been added; for should sulphite of lime so formed accompany the crystals it oxidises in the air, and acts very injuriously upon the charcoal filter. In some refineries, however, no such influence has been noticed.

In making sugar from the sugar cane the finished boiled juice was formerly brought into a reservoir, and allowed to cool to 45° or 50°; the mass of crystals and syrup was then put into a vessel with a perforated bottom, and the syrup allowed to drain away. At the present time, this imperfect method is almost completely abandoned. In most boiling houses the thick syrup passes into large shallow receptacles, where it is allowed to cool, and the crystallisation to proceed for twenty-four hours. The finishing of the crystallisation takes place in moulds, from which the syrup is run off through an opening at the end. Many sugar boilers have already introduced the centrifugal apparatus for the removal of the syrup, using a solution of sugar for the purpose.

The yield of 1,000 parts of sugar cane by the methods described does not exceed 55 to 65 parts of cane sugar; but the amount of sugar present in the cane originally may be taken as 160 to 190 parts. A part of the difference goes into the syrup, and part remains in the imperfectly pressed cane, the sugar being distributed in the following proportions:—

Sugar obtained in crystals	55 to 65 parts
Sugar in the syrup	25 to 20 „
Sugar remaining in the crushed cane	80 to 75 „

This considerable loss, amounting on the average to 56 per cent., is therefore principally due to the imperfect method of obtaining the juice. As an improvement, it has been recently recommended to disintegrate the cane similarly to the way in which the beet is treated, and to press the paste in hydraulic presses, adding ½ per cent. of the weight of cane of sodium sulphite, in order to prevent change in the juice. The use of sodium sulphite in Louisiana, where in consequence of the cooler climate, the cane is poorer in sugar and richer in foreign matters than in the West Indies, is said to have given good results. By a complete extraction of the juice, especially if the press residue be mixed with 15 or 20 per cent. of water and again pressed, a considerably higher yield is obtained; but it must be borne in mind that the crushed cane, the bagasse, or cane trash, is generally the only available fuel, and that probably this could only be very imperfectly replaced by the disintegrated press residue. When coal can be purchased, Robert's diffusion process is, on account of its simplicity, undoubtedly best adapted for obtaining an improved yield of juice.

Another essential improvement consists in boiling the sugar to granulation in the vacuum pan, by which means the formation of crystals of the largest size is promoted. After the crystallisation is finished, the crystalline sugar is brought into the centrifugal apparatus, and treated first with pure syrup and then with steam. A product is thus obtained which is fit for consumption without refining.

A new method of defecating cane juice has been introduced by Perrier, Possoz, and Cail. It depends upon the use of neutral sodium sulphite. The dried salt is dissolved in three times its weight of cold water, and the solution is added to the juice in the defecation pan, in such proportion that ½ to 1 part of the dry salt is mixed with 1,000 parts of juice. If the juice is not thus sufficiently clarified, a little milk of lime is used; but only enough lime is used to render the juice exactly neutral, without being alkaline. During the consequent defecation, the juice is boiled a short time and the scum is carefully removed. The further evaporation can be carried on either in open vessels or in vessels partially exhausted of air. This method has found acceptance in several colonies, and a large quantity of the salt is exported from France for the purpose.

Crystallisation and Working up of the After Products.—According to the quality of the juice, or the arrangements of the factory, the crystallisation yields either lump sugar (melis) or raw sugar. The former is only yielded by juice of good quality

carefully treated; the latter by any juice. Lump sugar always forms a hard mass of definite shape, resulting from numberless more or less well defined crystals, growing closely upon, and combined with one another. The raw sugar consists of separate, generally larger and better formed crystals, that do not grow upon one another. By a special operation, the syrup is completely removed from the lump sugar, which is not necessary to the same degree with the raw sugar.

Lump sugar can be prepared either from juice boiled blank or to granulation, but the latter is the one generally used. The juice boiled to granulation is to be considered as an intimate mixture of sugar crystals with blank boiled juice that crystallises upon cooling between already existing sugar crystals; it thus yields a denser mass of sugar than blank boiled juice, in which only so many crystals can form as may correspond with the degree of concentration.

In order to obtain lump sugar from juice boiled to granulation, the product of a boiling is allowed to flow from the vacuum pan into a spacious receiver, consisting of a large shallow copper dish with double sides. It is there heated by steam to 90° and passed into the crystallisation vessels, the well-known conically shaped moulds made of lacquered sheet iron. This reheating of the liquor has for its object to redissolve a portion of the crystals. All the crystals, however, do not dissolve equally; the smaller crystals presenting the largest proportional surface are chiefly dissolved, the larger remaining and forming the grain of the sugar. Upon cooling, the dissolved portion again crystallises between the existing crystals and thus forms a hard dense loaf.

In order to obtain this hardness with blank boiled juice, the formation of large crystals is prevented by stirring the mass from the commencement of the crystallisation. When intended for the preparation of lump sugar, it is boiled to a somewhat stiffer consistence. It is run into a large receiver, similar to that just described, but called the cooler, as in this case the liquor is not reheated, but left to crystallise, being meanwhile vigorously stirred with a wooden spatula and after some time it is run into the moulds.

The further treatment of the lump sugar in the moulds is the same as in the operation of refining, which is described on p. 863.

In the preparation of raw cane sugar various crystallising vessels are used, either of the same conical shape as for lump sugar, but three or four times as large, or large rectangular or pentangular chests, or a large vessel capable of receiving a third of the entire boiling. These stand in a room heated to 28° or 32°. The size and sharpness of the crystals are dependent upon their forming very slowly, and having time to grow, and this can only be accomplished by a very gradual cooling. The more rapidly the liquor is cooled the smaller are the crystals, and the presence of non-crystallisable matters has a similar effect. From a specially good juice comparatively large crystals are obtained even with rapid cooling, whilst an inferior juice under similar conditions only hardens to a pasty mass. The size of the crystallising vessel has also an influence upon the crystallisation, small moulds being used for good juice, and large ones for inferior juice. The time required for the completion of the crystallisation depends on circumstances; with good juice in small moulds it is finished in six to eight hours, the larger ones take twenty-four to thirty-six hours.

The mother liquor or syrup is drained off from the crystals in the cones, by removing a plug from the apex; the chests are inclined so that the syrup can run off over the brim; and the larger vessels are provided at the bottom with an opening. The syrup flows off gradually, but more quickly the higher the temperature of the room and the purer the juice; several days are, however, always required. Even after the draining is ended the sugar is never quite free from syrup, the separate crystals retaining some by surface attraction and capillary action. This is removed by liquoring, or by centrifugal action. The liquoring, which is confined to the cone-shaped vessels, is carried out by pouring upon the sugar in the broad upper portion of the mould either pure water or a solution of purer sugar. The water dissolves a portion of the sugar, and becoming saturated, percolates through the mass of crystals, driving before it the adhering syrup. The operation is repeated a second or third time, until the remaining sugar is sufficiently pure. It is immaterial whether pure water or sugar solution is used for the liquoring; in the former case the solution being formed at the cost of the sugar operated upon. This operation is best carried out in the conical moulds, as the liquid has there to traverse the greatest distance. After the last liquor has completely run off, the moulds are removed from their frames and emptied, by reversing them and striking their broad ends once or twice on the floor, by which the more or less adhering mass of sugar is jerked out. It is then broken up with a mallet, and passed between toothed rollers, after which it is ready for the market.

The liquoring of the sugar in moulds takes a very long time, as the syrup drains slowly, necessitating the use of a great many crystallising vessels and the occupation

of much space. This difficulty is completely overcome by the use of the centrifugal machine, which has now been introduced into most sugar manufactories. In many

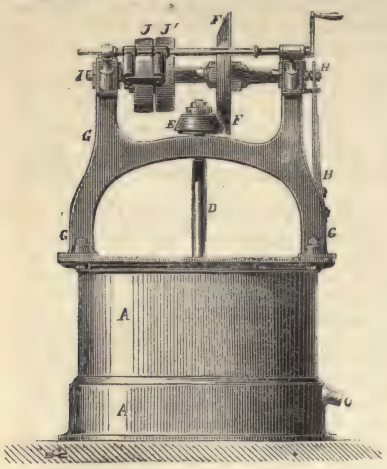


FIG. 625

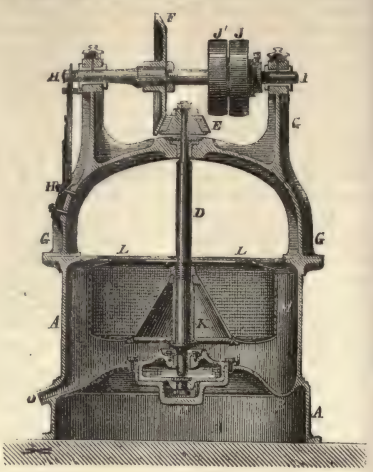


FIG. 626.

places its use is confined to the after products, but in others it is applied to the first product. A section of the centrifugal machine is shown in fig. 626; its external appearance in fig. 625; as seen from above in fig. 627; and some of the details in fig. 628. It consists of two concentric hollow vessels: the outer one (A), which is made of cast iron, is intended to receive the syrup and has an opening (O) through which it can be run off; the inner one (L L) which holds the sugar mass, is made of strong perforated sheet iron or copper, and is covered inside with a fine wire sieve. This inner vessel, the drum, is driven by means of the cone (K) and the vertical shaft (D) with which it is connected. The shaft passes through a stuffing box into the hollow bearing (C) below, and its extremity rests upon a ground steel plate; to diminish the friction the hollow bearing is filled with oil. On the edge of the outer vessel, or jacket, is fastened a strong iron arch (G G) which supports the driving mechanism. The shaft passes through a bush in this arch, and has at its upper end a friction cone (E), formed of a disk of leather closely pressed together; upon this acts a conical friction wheel (F), fitted on a horizontal shaft (H I), and pressed by a spring (H H) against the cone, the degree of pressure being regulated by screws in the springs. Over the pulley (J), which runs loose upon the shaft (H I), is the driving strap (H, figs. 627, 628), which when the machine is to be set in motion is pushed by an arrangement, shown in fig. 627 (enlarged in fig. 628), upon the strap wheel (J″), which is fastened to the shaft. A bar (*a b*, fig. 627; A B, fig. 628) lies parallel over the shaft (I H), and supports near its ends two forks, between which the driving strap runs. This bar being fitted in a female screw, when turned by a handle (E) slides to or fro in a horizontal direction; the driving strap is thus pushed off or on to the loose pulley (J), and

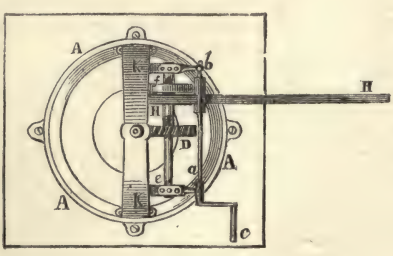


FIG. 627.

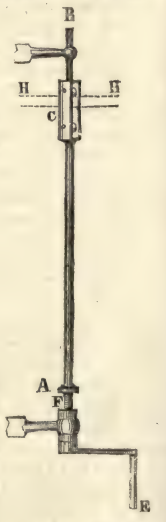


FIG. 628.

the drum is made to revolve or stopped at will. A modification of this apparatus has been made very generally in the placing of the driving machinery beneath the drum instead of above it; this gives greater convenience in filling and emptying. The drum has a diameter of 32 inches and is 13 inches deep; it makes about 1,200 revolutions per minute.

After the crystallisation of the sugar has ended, the entire contents of the chest, without first removing the syrup, is emptied into the crushing machine, a horizontal iron trough, in which numerous blunt knives revolve in a vertical direction. These break up the sugar mass, and mix it with the syrup. The result should be a uniform moderately fluid paste; should the syrup present be insufficient to give it the desired liquidity, sufficient from another operation is added. This paste is ladled into the drum whilst in full rotation; it is at once flung by the centrifugal force against the side, where the sugar is retained by the sieve, whilst the syrup flows through into the jacket. In a few minutes the sugar is freed from all but a small quantity of the syrup, which is separated by a liquoring operation. A small quantity of clear syrup is thrown into the drum; this penetrates at once through the sugar mass, and is driven off by the centrifugal force. After a second similar liquoring, the sugar is usually pure white. The syrup that flows off from the second liquoring can be used in the next operation for the first liquoring. The entire operation including two or three liquorings is finished in eight or ten minutes. When the ordinary moulds are used, and the syrup allowed to drain, the operation takes several weeks, according to the quality of the product.

The syrup that runs off from the first product is still a saturated sugar solution, of course rendered impure by the non-saccharine matter that was previously contained in the whole of the juice. In order to obtain this sugar, it is again boiled in a vacuum to string proof and left to crystallise. The product is purified in the centrifugal machine, and the syrup driven off is again boiled, and yields a third product. The syrup from this still contains about half its weight of crystallisable sugar, but the non-saccharine matters have now become so concentrated that no more crystals can be obtained by a fresh boiling. It is therefore collected in large cisterns, when after standing for months some crystals gather at the bottom. The supernatant liquor, or molasses, is removed as far as possible by skimming, and ultimately the crystals are placed in the centrifugal machine and yield a last product. The molasses still always contains about 45 per cent. of sugar, and some methods will be described having for their object the obtaining of this sugar; generally, however, the molasses is not worked further, but used in the manufacture of spirit.

Working up of By-Products.—The by-products of the manufacture of sugar from the sugar cane consist of the scum, the pressed cane (bagasse or trash), and the syrup. The scum, which is produced only in small quantity, is used as manure. The trash is used as fuel for heating the evaporating pans; the ash which it yields is unusually rich in potash, and could be used in the glass manufacture; but it is preferable to restore it to the soil in order to provide nourishment for the succeeding crop. The syrup goes partially into the market, and being free from the disagreeable smell of beet syrup, and containing a smaller amount of salts, is fit for direct consumption. The larger portion is worked in the West Indies, after fermentation, for the preparation of rum and alcohol. Generally it is allowed to ferment with the juice of the damaged canes, and a rum is thus obtained which is especially liked for its fine aroma.

The following represents the plant of a sugar-boiling house capable of working 10,500 gallons of juice daily, or nearly 1,600,000 gallons in a season of 150 days, producing about 1,200 tons of sugar.

The steam power is equal to about 92 horse power, of which 16 horse power is used for driving the machinery, and 76 horse power for the evaporation. For the defecation six pans, 4½ feet in diameter, are provided; each holds about 220 gallons of juice, and makes eight operations daily, or altogether 48 operations. From 5 to 10 ounces of lime are used for each defecation. The filtration requires eleven filters, each containing 1¼ tons of animal charcoal, or altogether 13¾ tons. Six of the filters filter about 88 gallons of thin juice hourly, or in the twenty-four hours, including four hours' rest, between 10,000 and 11,000 gallons. Five filters used for thick juice yield about 4,400 gallons daily. Every twenty-four hours two filters are freshly filled. The charcoal from each filter retains about 12 cwts of thick juice; this is first displaced with thin juice, and then the thin juice is washed out with water until the liquor flowing away is of sp. gr. 1·013. The washing of the filter lasts three hours. The evaporation is effected first in three systems of condensation pipes, and then in two vacuum pans; the first of them exhausted to 12·5 inches and the second to 6·5 or 7 inches. In the crystallisation the syrup is heated to 80°, and yields then 160 moulds each containing about 150 lbs. of mass; after draining there remains about 110 lbs. of sugar in each mould. The daily product of sugar would therefore be nearly 8 tons.

Working of the Scum.—The different scums produced in the defecation and saturation are permeated by a large quantity of juice, in proportion to the voluminousness of the precipitate. Formerly, to recover this juice the scum was filled into linen bags, the juice allowed to drain as much as possible, and the bags then placed in the hydraulic press. This was the most disagreeable and uncleanly operation of the whole manufacture. The larger quantity of lime scum produced by the modern methods of defecation has rendered this method impracticable, and a great advance in the sugar manufacture was made by the introduction of the filter press used by Needham, for the removal of water from clay in the porcelain manufacture. This he



Fig. 630.

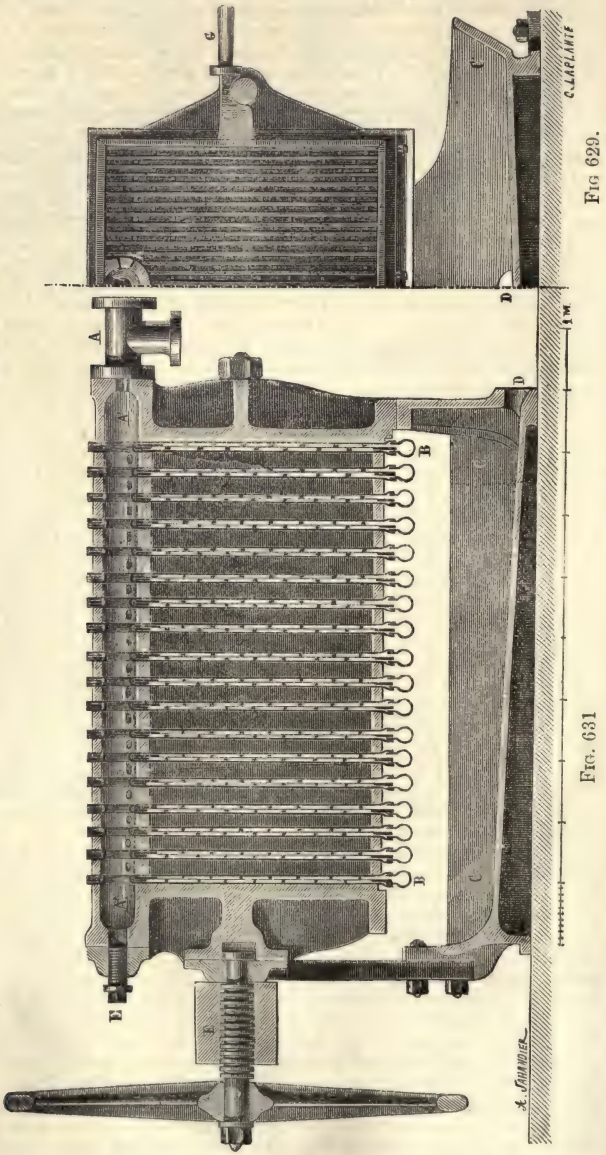


Fig 629.

Fig. 631

afterwards adapted to the requirements of the sugar manufacture, and at the Exhibition in London in 1862 he produced the sugar scum press. Since that time it has

been several times modified and improved by Danek of Prague, Trinks of Helmstadt, and Riedel and Kemnitz in Halle.

The filter press may be described as consisting of very narrow, tall, and broad chambers, the two tall and broad sides of which are formed of willow rods laid perpendicularly and covered with linen. In the upper narrow end is an opening, into which is set a very tall pipe. When a slimy liquid is poured into this pipe, the water at first passes easily through the linen covering the sides, and no other way being open it follows the direction of the rods. The sides soon become covered with a dense layer of scum, which would prevent the flow of the liquid were it not for the pressure exerted by the column of liquid in the long pipe, which drives out the water until the chamber is full of dense scum from which the water has been driven out. A filter press consists of eighteen or more of these chambers, the four closed sides of which are formed by planed iron frames. The wicker work is now imitated by two thin iron plates, perforated by long slits, which are so arranged that when the plates are placed against one another there is a communication between all the openings. The plates are covered with linen, and the chambers thus formed by the frames and plates being filled with scum, the liquid runs through into the connected slits, and escapes between each pair of frames, leaving the scum in the chamber. The long pipe is filled by a monte-jus which is in connection with all the chambers. One modification of the filter press is shown in figs. 629 to 631. Fig. 630 is a vertical section through a chamber showing the iron plates forming the sides with the longitudinal openings. In the middle and near the upper edge is a circular opening. Each pair of plates is covered with linen, and between each pair is an iron frame (A′) with a circular opening exactly corresponding with the circular opening in the plates, so that when pairs of plates and frames are placed alternately, a corresponding number of chambers are formed, which are connected by a common channel formed by the circular openings in the plates and frames. The sides of the opening in each frame are perforated several times in an oblique direction, so that the channel is thus placed in communication with the interior of each chamber. This is shown in fig. 629, which represents a section at right angles with that in fig. 631. The frames are suspended on a strong iron frame, each being provided with two projections (G), that rest upon an iron balk. The eighteen frames are pressed closely together by means of a strong screw (F, fig. 631) until they are watertight. The complete press is shown in fig. 631. The pipe (A) leading from the monte-jus is connected with the end of the press; its prolongation (A′) is formed by the circular openings in the frames and plates, and at the opposite end it is closed by a screw (E). The frames and plates are secured by the pressure of the screw (F) upon the end piece of the press. The filtered liquid runs through the openings in the plates into the trough (B), and thence into the iron reservoir (C), from which it is run off at (D).

The scum to be filtered is worked up into a uniform mass, then run into a monte-jus and driven under steam pressure into the filter press. The removal of the liquid takes place very quickly, and the press remains filled with a dry cake of scum. To empty the press the screw (F) is loosened and the end piece withdrawn; the frames and plates are then lifted out successively, and the intervening scum cake removed, until the press is emptied. The plates are covered with clean cloths, and returned with the frames to the press; the screw is applied, and the press is ready for a fresh operation.

The suggested modifications of this apparatus have been very numerous, but the principle remains the same in all.

Working of the Molasses.—The liquor from the last crystallisations, known under the name of molasses, is a solution of crystallisable sugar, in which however crystallisation is prevented by the presence of a large proportion of foreign matters. Its composition evidently varies with the quality of the juice, but on an average molasses contains 50 per cent. of crystallisable sugar, 30 per cent. of non-saccharine bodies and 20 per cent. of water. Upon incineration the non-saccharine matter yields 3 parts of ash. To separate this large quantity of crystallisable sugar different methods have been proposed. Some of these are based upon the fact that sugar will form insoluble compounds with the alkaline earths, which can then be separated from the soluble non-saccharine matters; another method depends upon the osmotic behaviour of molasses.

Dubrunfaut has introduced a method based upon the insolubility of sugar baryta. The molasses is diluted with boiling water, and whilst hot mixed with so much solution of barium hydrate as contains one molecule of baryta for each molecule of sugar. A flocculent precipitate of sugar baryta is immediately thrown down, whilst the remaining matters, or at least the greater part, remain in solution. The sugar baryta is washed with hot water until all other matters are removed, an operation in which the filter press may be used with advantage, and it is then suspended in water and satu-

rated with carbonic acid. The carbonic acid decomposes the sugar baryta, forming insoluble barium carbonate, whilst the sugar is set free. The precipitated barium carbonate is freed from sugar in a filter press, and by ignition with charcoal it can be again converted into barium hydrate, so that the same quantity of baryta can be repeatedly used. The saturation must be effected at the temperature of boiling, to avoid the formation of acid barium carbonate. Even when this is accomplished, some baryta always remains in solution. As barium acts poisonously upon the system, this must be completely removed; the juice is therefore filtered through animal charcoal, upon which is placed 2 parts of calcium sulphate or gypsum, or an equivalent quantity of sulphuric acid (sp. gr. 1·49), for every 1,000 parts of the prepared molasses. The latter treatment, however, does no good to the animal charcoal.

Another method, in which baryta with its disadvantages is replaced by lime, has been invented by Scheibler. Each 100 lbs. of molasses is thoroughly mixed with about 27 gallons of 82 to 85 per cent. spirit and 37 or 38 lbs. of lime. A sugar lime compound is produced that is completely insoluble in spirit, whilst the non-saccharine matters remain dissolved. The alcoholic solution is separated from the sugar lime in the filter press, and the sugar lime is washed with alcohol; the alcoholic solution and washings being afterwards submitted to distillation to recover the alcohol. The sugar lime still saturated with alcohol is placed in a saturator connected with a distillatory apparatus, and heated with water to boiling, while at the same time carbonic acid is introduced. The alcohol distils off from the boiling liquid, whilst the sugar lime yields calcium carbonate and crystallisable sugar.

The osmotic treatment of the molasses is essentially the same as the diffusion method of separating sugar from beet previously described, but in this case the natural diffusion organ, the membrane of the vegetable cell, is replaced by an artificial one of parchment paper. The parchment paper is stretched over the edges of shallow frames, a number of which, filled alternately with water and molasses, are fastened together, and diffusion then goes on between the water on the one side, and the molasses on the other. The constituents of the molasses are diffusible in very different degrees; the sugar, although a crystalloid, diffusing more slowly than the salts and some of the other organic substances. The greater part of the salts can therefore be obtained in the outflowing water, but also with a loss of a certain quantity of sugar, the amount depending upon the way in which the operation is carried out. When the water diffuses rapidly, little sugar is taken up; but when it is long in contact with the molasses, a proportionately larger quantity of sugar is carried through. An absolute separation of sugar and salts by this method is not possible, the most that can be done is to reduce the proportion of salts. But as it has not been shown that the presence of the salts hinders the crystallisation of the sugar, and it is much more probable that this is dependent on the presence of non-saccharine matters, it is not likely that all the sugar can be obtained in a crystalline form in this way. Practically, only about 15 per cent. of a very impure dark-coloured sugar is obtained from molasses containing 50 per cent.

It has been recommended by Champonnois, and afterwards by Payen, that the syrup from the first product should be mixed with fresh beet pulp in such proportions that the pulp produced in a day should be used up with the syrup made the previous day. The syrup is first diluted with water to the concentration of the normal juice, heated to 70°, added to the pulp brought to the same temperature, defecated by the Perrier-Possoz method, and afterwards worked in the ordinary way. A coagulation of the albumin and a considerable absorption of the salts by the substance of the pulp is said to take place; consequently the constituents of the beet, with the exception of the sugar, would be retained in the pressed pulp and the juice would be considerably purified. All working of the after product would be done away with, as only first product and no molasses would be produced. It has yet to be proved that this method can be practically carried out, but experiments by Bodenbender have shown it to be very improbable that the beet pulp has such an absorbent action upon non-saccharine matters.

The whole of the by-products and refuse of the beet-sugar manufacture find useful application as fodder, manure, or in other ways. They consist of the beet leaves and tops, the pressings, residues from the centrifugal maceration or diffusion operations, the washing, defecation, and saturation scum, the refuse from the washing of the charcoal, and lastly the molasses.

The beet leaves are generally used with least advantage, being simply thrown upon the land and there allowed to rot. Sometimes they are used as fodder, and during the beet harvest the yoke oxen are fed exclusively upon them. This is almost equally irrational, for though on account of their richness in albuminoids, they form good fodder when given in suitable quantities, in large quantities they produce purging and weaken the beasts.

The leaves are also used after being buried in pits, and there allowed to ferment. Immediately after the harvest, the leaves are stamped into brick or simple earth pits, so as to lie close and enclose but little air and are then covered with earth. Fermentation commences almost immediately and continues for a long time. The leaves are kept in this condition till the following spring or summer. The parts round the edges and the top layer are usually overgrown with mould and have to be separated. As soon as the principal fermentation is over the leaves may be used for fodder; the peculiar smell that the leaves acquire is at first distasteful to the beasts, but after a short time they become habituated to it and take the fodder willingly. The value of the leaves is dependent upon their remaining green at the time they are gathered.

The beet tops are always worked up into fodder with the pressings and other residues from the juice winning operations. They are placed in alternate layers in large brick pits, pressed down, and then treated in the same way as the leaves. They immediately commence to ferment and acquire an agreeable faintly acid smell, and the beasts eat them greedily. If the juice has been imperfectly removed, and much sugar is left, a considerable quantity of free acetic and lactic acid is formed during the fermentation. In this case there is not only loss of sugar, but the consumption of such sour pressings in any quantity affects the beasts injuriously. The fermented pressings should only have a faintly sour taste and slightly redden blue litmus paper.

The residues from the juice extraction form a poor fodder compared with albuminoid substances, but rich compared with easily digestible non-nitrogenous matters. Mixed with substances rich in albumin, such as oil-cake or beans, they form a good fattening food for cattle and sheep.

The residue yielded by the various methods of obtaining the juice differs considerably in composition, especially in the amount of water it contains. That from the hydraulic presses contains most dry substance, about 30 per cent.; that from the centrifugal machine contains only half as much; that from maceration by Schutzenbach's method usually 16 to 20 per cent., but more or less according as it is pressed. Finally, the diffusion residue only contains about 8 per cent., and sometimes only 4 per cent. of dry residue; in the latter case the water is allowed to drain off until the dry substance reaches about 8 per cent. before burying it in the pits.

The following analyses of the residues of different factories will show the composition of the pressings and diffusion residues:

Pressings (Stohmann).

Albumin	2·36	2·41	1·43	2·11
Fibre	6·86	5·72	4·15	4·90
Fat	0·38	20·03	0·13	0·19
Non-nitrogenous extract	17·30		14·60	18·42
Mineral matters	3·05	3·40	4·36	2·51
Water	70·05	68·44	75·33	71·87

Diffusion Residue.

	Stohmann		Von Wicke.	
	Fresh from diffuser.	From the pits.	Pressed by Schottler's press.	
Albumin	0·74	0·60	1·29	0·76
Fibre	1·46	2·24	3·06	2·18
Fat	0·06	0·03	0·16	0·15
Non-nitrogenous extract	4·20	5·22	5·72	6·90
Mineral matters	1·64	1·74	3·53	2·90
Water	91·90	90·17	86·24	87·11

The wash residue from the beets, the refuse beets, and the scum from the filtration, defecation and saturation, the latter containing much lime, can be made into a good compost. The defecation scum is usually overrated as a manure, the organic substances in it containing on an average only 0·5 per cent. of nitrogen; of other plant foods, with the exception of lime, it contains only about 1 per cent. of phosphoric acid. But on soils poor in lime and heavy clayey soils the beneficial action of the compost on account of the lime it contains cannot be denied.

The refuse of the charcoal washings is carefully collected in settling basins; at the end of the season the charcoal slime is either converted into superphosphate or sold to the manure makers.

The molasses is used in the spirit manufacture, or when the market price is low it may be used for feeding cattle if given with a proper proportion of albuminous fodder. The latter method has the advantage that the greater part of the mineral constituents of the beet is returned to the soil in the dung.

The Effluent Water.—In all parts of the manufactory foul water is produced, laden with more or less organic and fermentable substances. When this is allowed to run into the streams and ditches it supports the growth of a large quantity of slimy algæ. One of these, the *Beggiatoa alba*, has the property of decomposing the sulphates, which are present in all waters, with the liberation of sulphuretted hydrogen, killing the fish and giving rise to foul smells. If there be meadow land in the neighbourhood of the manufactory, the injury to the streams may be avoided by using the effluent water for the irrigation of the land, and thus purifying it before it flows into the watercourses. Where there are no meadows an artificial disinfection has to be effected.

Suvern's disinfectant consists of milk of lime prepared by slaking 100 parts of lime with water, and during the effervescence adding 7½ parts of coal tar and 15 to 20 parts of magnesium chloride. This milky mass is allowed to flow in a thin stream into a narrow canal through which the whole of the foul water from the factory flows. When the turbid water and milk of lime meet, a flocculent precipitate is formed. The water passes through a canal 100 to 150 ft. long, and through two large basins successively; in the second basin the deposit of the precipitate is completed, and the water flows from thence clear. The addition of the milk of lime must be so regulated that the effluent water has a distinctly alkaline reaction. Through the addition of the lime dissolved matters are precipitated in an insoluble form, the precipitate carries down mechanically all suspended matters, together with organic germs, whilst the alkalinity of the water destroys all vegetation of the lower organisms. The water is thus at a small cost sufficiently purified to be allowed to run into the streams without injuring them. Whether the coal tar and magnesium chloride are necessary is very questionable; probably pure lime is sufficient. The precipitate obtained by this method in three different factories in Saxony had the following composition (Stohmann):—

Phosphoric acid	0·37	0·18	0·20
Nitrogen	0·12	0·16	0·09
Potash	0·23	0·21	0·06
Lime	6·23	9·17	6·56
Alumina and ferric oxide	2·64	2·40	1·37
Sand and earth	26·05	24·29	10·64
Water	56·98	55·15	75·69
Magnesia, carbonic dioxide, chlorine, etc.	7·38	8·44	5·39

The disinfection scum may be advantageously incorporated with the compost previously described, the quality of which should be improved by the lime it contains.

Sugar Refining.—Neither the cane sugar from the plantations nor that prepared from beet comes in any considerable quantity directly into consumption; by far the greater portion is worked up again in special establishments, the Refineries, and converted into a purer white product.

The object of the refining is to remove from the sugar mechanical impurities, such as sand, earth, splinters from the casks and chests in which the sugar was packed, particles of crushed cane, colouring materials, uncrystallisable sugar, and albumin; different salts, such as potassium chloride and nitrate, sodium chloride, calcium carbonate, phosphate and malate, and magnesium phosphate. In sugar from the tropics, free acids are present, such as malic acid, pectic acid, acetic acid, and lactic acid, the two latter being products of fermentation, which easily takes place in these kinds of sugar in the stores or on board ship, and these acids give rise to the formation of grape and fruit sugar. In beet sugar these changes do not take place, if the juice be kept alkaline during the working; on the other hand, there is always then a residue of sugar lime.

In establishing a refinery, it is necessary to secure a sufficient supply of the purest possible soft water; it should also be within reach of good and cheap fuel.

Formerly the value of cane sugar was judged exclusively by external characters: the form of the crystal, the grain, the colour, and the smell. This however no longer suffices, and the amount of pure sugar is now accurately determined by the saccharometer, as well as the amount of moisture and non-crystallisable sugar. Only with a knowledge of the sugar contents, and of the proportion between the crystallisable and non-crystallisable sugar, is it possible to make an accurate estimate of the yield to be expected.

The better qualities of cane sugar have well formed, distinct crystals, and a close grain; they are white or of light yellow colour, and feel hard and dry (soft white sugars are imperfectly freed from syrup). They should not have an acid reaction, for that indicates partial decomposition; on the other hand, a strong alkaline reaction is not desirable, as it would be due to a great excess of sugar lime.

Generally the colonial sugar, prepared from juice containing grape sugar, and defe-

cated without an excess of lime, is more or less altered during transport, and it feels sticky to the touch; it has then less grain, forming smaller crystals than beet sugar. Beet sugar, if well prepared, if not over boiled, or too rapidly crystallised, and consequently containing too much syrup, is easily refined, and gives a high yield of white cane sugar. It is therefore preferred to the colonial sugar, except that of the best qualities, notwithstanding that the syrup obtained as a by-product from the latter is more easily disposed of.

As the sugar refiner is compelled, in order to meet his requirements, to purchase sugar of the most diverse qualities, care has to be taken to assort it immediately upon its reception, so that afterwards it may be worked up either with sugar of the same quality only, or with a suitable mixture of different qualities. Thus colonial sugar is sometimes mixed with beet sugar, in order to neutralise the alkalinity and the disagreeable smell of the latter with the acidity and better aroma of the former.

The whiter kinds of colonial sugars are usually reserved, in order to use their solution for liquoring the refined sugar; they are seldom refined, being sought for, for the preparation of the finer products. On the other hand, they are often used for the preparation of fruit syrups, confectionery, etc. The finest beet sugar, containing 98 per cent. of sugar, is also used for the finishing of the syrup.

The refining includes the following operations: the storing of the cane sugar, the emptying of the casks or running of the sugar, the solution or melting and clearing, the filtration, the boiling, the crystallisation, the draining of the syrup and claying, the drying, and finally the treatment of the syrup.

Storage.—The sugar is brought at once into an airy, dry room, the well-boarded or cemented floor of which slopes to one side, so that the syrup draining from the sacks or casks flows off into a reservoir. The casks are piled upon one another according to their size, care being taken that the best and strongest casks are underneath.

At the commencement of the refining the casks are emptied near to the solution apparatus, the thick hard pieces which always occur being picked out and broken up by themselves. A certain quantity of sugar always remains adherent to the side of the cask, and this is best recovered by solution in condensed steam. For this purpose a hollow brickwork chamber corresponding to the size of the cask is provided, which is lined with copper, and has a steam pipe in the centre. The cask is placed bottom upwards over the steam pipe, and an iron bell hanging from a pulley is then let down over the cask. Upon opening the steam pipe, the cask is filled with steam, which condenses upon the cold sides; the water dissolves out the sugar, and the syrup collects at the bottom of the chamber. The wood of the cask is softened by the steaming out, and after the removal of the bell, it is in a suitable state for repairing, re-hooping, etc.

The sugar emptied from the casks is thrown upon a sieve, and the lumps that do not pass through are broken up between a pair of toothed cylinders, or a suitable mill.

Melting and Clarification.—The clarification or separation of all mechanical impurities and a portion of the dissolved foreign matters from the syrup obtained by dissolving the sugar, is effected by means of finely powdered animal charcoal and a solution of albumin. The albumin being added to the syrup at a low temperature is distributed through it equally; upon heating the syrup, the albumin coagulates in flocks, which enclose within them the foreign matters and the mechanical impurities, as well as the animal charcoal that has been added. When a sour colonial sugar is being worked, sufficient milk of lime is added at the same time to give it a very faint alkalinity. But this is avoided when possible, and it is preferred to work a mixture of colonial and beet sugars, so as to neutralise the acidity of the one with the alkalinity of the other.

Generally the albuminous liquor used is the blood of cattle and sheep, from which the fibrin has been separated by beating it with rods immediately after the slaughter of the beasts. It is preserved in sulphured vessels, or with an addition of sulphurous acid or sodium sulphite. In consequence of the rapidity with which blood commences to putrefy, and the unbearable stink thus produced, its use is very offensive, but the use of a small quantity of sulphurous acid retards the process of decomposition considerably. Robierre and Dureau recommend that the blood should be mixed with double its weight of animal charcoal and dried at a low temperature, preferably in a current of air heated to not above 55°. In this dried condition the blood can be preserved, and its action is equal to that of the fresh. Blood dried without the addition of charcoal is at present a commercial article, but its use in this form would probably be too expensive.

In many refineries the use of blood has been either entirely given up or limited to the working of specially slimy sugars. The clarification is then replaced by a proportionally more careful treatment of the filters.

The clarifying pans have generally the same construction as the defecation pans of the beet-sugar manufacture. They are placed sufficiently high to allow the syrup to run from them directly into the filters. The water for effecting the solution, about 50 parts of water to 100 parts of sugar, is run into the clarifying pan and heated. The sugar is then shovelled in, and the first melting is effected with continual stirring; powdered animal charcoal is added in the proportion of 5 parts to 100 parts of sugar, and by vigorous agitation distributed throughout the entire liquid. To the lukewarm juice is then added 1 to 2 parts of blood that has previously been mixed with five or six times its volume of water; the whole is again well stirred and then boiled. When the black coating of scum is broken through by white bubbles it is an indication that the clarification is effected. The liquor is next cleaned from scum by a first filtration, the turbid portion first flowing off being returned to the filter, and the clear liquid passes to the charcoal filter.

Filtration.—As preliminary filters the old Taylor's filters are generally used. They consist of strong wooden copper-lined chests, 3 to 6 feet square and 20 inches high. The front side is formed of a door. Over this is a still larger chest, also of wood and copper lined, but only 6 inches high. In the bottom of this 24 copper pipes are fitted into as many holes, about 2 inches in diameter. The pipes are sufficiently long to project an inch or two into the under chest. At the lower end is a rim, and above this a ring opening with a hinge and tightened by a screw; by means of these rings the filtering bags are fastened to the pipes. The filtering bags are made of linen, and are 40 inches long and 20 inches in diameter; each of these is enclosed in a second bag 8 inches in diameter, but of loose texture. By thus putting a broad into a narrow bag numerous folds are formed, and the filtering surface correspondingly increased.

The juice with the scum flows from the clarifying pan into the upper chest, and from this through the short pipes into the bags fastened to them, in which the scum is retained; from these it passes through a pipe fixed in the bottom of the lower chest into a trough by which it is conducted away. As the removal of the slime from the filter is a rather difficult operation, the filtration in many refineries is reversed; instead of filtering from the inside to the outside, the filtration is effected from the outside to the interior, so that the slime is retained in the spaces between the filters.

Another method is to use a rectangular copper-lined wooden chest, open above, 40 inches wide, 52 inches long, and 80 inches deep. The chest is provided with a false bottom, in which are a series of wide openings having copper pipes as in Taylor's filter, but in the reverse direction, so that they project upwards. Below the false bottom is the proper one, from which the filtered liquid is run off by means of a tap. The filtering bags are fastened to the copper bags with their mouths opening downwards, a strong bent wire being previously placed in them to keep their sides apart. The separate bags are supported by cross pieces fastened to the sides of the chest. The syrup to be filtered is run into the chest, when the slime remains between the separate bags, whilst the clear liquor enters them and flows off through the pipes. The slime can then be easily removed from between the bags, especially if the pipes are unscrewed and the bags lifted out. In continual working this is only necessary when the entire chest is filled with slime. The residue is stirred up with water and boiled; the liquor is afterwards allowed to settle, and when clear is drawn off and replaced by fresh water, and this is repeated until it no longer takes up much sugar. The wash water containing sugar in solution is used instead of water to dissolve a fresh quantity of sugar. The slime is finally pressed and sent to the manure factory, where by treatment with sulphuric acid it yields a nitrogenous superphosphate.

The preliminary filtration has for its object to save the charcoal filters, and to separate the matters mechanically retained in the coagulated albumin. The hot syrup flows directly from the preliminary filter on to the real filter, which is arranged exactly as described under the beet-sugar manufacture. Generally two filters are used together, the syrup passing from one to the other, and a filter being used as long as the syrup passes from it perfectly colourless.

When foul the filter is cleansed with boiling water; the first liquor, so long as it is sufficiently concentrated, being added to the other syrup, and the more dilute liquor is used like the wash water from the preliminary filter for dissolving fresh sugar. As the charcoal of the refinery takes up far less foreign matters, its revivification is much more simple. When the water flows from the filter pure, the charcoal is steamed in the filter itself, dried, and then brought to a red heat. After a time, a considerable quantity of lime salts accumulates, and a treatment with acid is necessary.

Boiling.—In the boiling of the syrup, vacuum apparatus similar in construction to those used in the boiling of the thick juice in the cane-sugar manufacture are now used probably without exception. As in sugar refineries they have to do with nearly pure sugar solution, it is boiled until it commences to grain, and the crystallisation is

allowed to begin in the vacuum pan. The finished syrup is then brought into the heater, and is there heated to 80°, in order to melt the greater part of the small crystals, the sugar from which runs between the larger crystals and forms a combination between them. The heater is usually sufficiently large to unite in it several fillings of the vacuum pan, and by their mixing these yield a large quantity of uniform products. After sufficient heating the steam is turned off in order to allow the crystallisation to proceed. By repeated stirring the formation of a conglomeration of crystals is prevented, and the granulation made uniform.

The Filling.—Usually the heater stands in the filling room, for convenience in filling the forms. A spacious trough runs through the wall of the filling room from the vacuum pan to the heater, and the syrup flows immediately from one to the other. The filling room is a large chamber, with a well-boarded level floor, so that any sugar spilt may be easily collected, and that the moulds may stand up regularly.

The following utensils are here used:—

Filling basins, for the removal of the syrup from the heater to the forms. These are round or oval copper flat-bottomed basins with wide spouts, provided with iron handles for convenient transport.

Large copper hemispherical ladles, 10 inches in diameter, provided with long handles These are used for the removal of the syrup from the heater into the filling basins. Spatulas or stirring knives, for stirring the syrup in the forms. These are of beech-wood, 4 feet long, the upper third forming the round handle; the spatula itself is knife-shaped, sharpened on both sides, 1½ inches wide, and ⅜ inch thick.

The moulds have the well-known conical shape of the sugar loaf. Formerly the moulds were generally made of burnt unglazed earth, protected from breaking by wooden hoops; at the present time these have been entirely replaced by moulds made of sheet iron. At the apex of the mould there is a small opening through which the syrup can drain away. To protect them from rusting, the moulds are coated with oil colour and varnished with a good siccative. As soon as the coat becomes injured at any part it must be renewed, as otherwise the sugar would be injured by rust, and moreover it would adhere to the mould.

The size of the moulds varies exceedingly, being influenced by the custom of the consumer and the quality of the product. For the finer kinds of refined sugar the smaller are used; for those prepared from the after products the larger ones are taken.

Before the filling of the moulds the opening in the head is stopped up with a plug of linen rag, and the inner surface is wiped with a damp sponge, the moisture remaining from which prevents the close adherence of the crystals to the side. The moulds are then placed upright, with the wide end upwards, side by side and resting against each other, the outside now being prevented from falling by an equal number of heavy cast-iron moulds standing on their broad bases.

During the filling of the moulds the syrup is carefully stirred with a large spatula in order to distribute equally the large crystals that may have sunk to the bottom. The filling basin is placed on an iron stand close by the side of the heater, so that its upper brim is on a level with the brim of the heater, and filled with the ladle; it is then carried to the mould and emptied, so that at first the moulds are only half filled. When this is completed they are filled in the same order to within ½ inch of the brim. This filling is carefully performed in two, or frequently three, operations, in order to distribute uniformly through the whole of the moulds the crystals, which continue to form in the heater during its emptying; otherwise the moulds would contain sugar of different grains.

A short time after the filling the mass becomes covered with a crust of crystals. This is the time chosen for the first stirring, the object being to raise the large crystals that have sunk through the still soft mass into the head of the mould and distribute them equally. This is done by thrusting the spatula into the sugar with its flat side against the side of the mould, and then drawing it rapidly in a perpendicular position upwards towards the centre. This is repeated several times, taking care to stir the sugar in a different place each time, in order to carry into the middle the crystals that are deposited by more rapid cooling on the sides. The right time for stirring must be carefully judged, as if it takes place whilst the mass is still too hot the grains again sink down through the thin liquor; whilst if it be effected too late a striped loaf is the result through the unequal distribution of the granules. A short time after the first stirring the spatula is again drawn through the mass twice.

The temperature of the filling room should be kept as uniform as possible between 30° and 35°, so as to avoid too rapid cooling of the forms. Above all strong draughts must be prevented, as these cause an unequal cooling, and consequently an unequal crystallisation.

The further operations are carried on in the sugar floors, which occupy the upper part of a refinery. They are large rooms, not more than 6 feet high, in order to economize space and heating material, and well floored and well lighted. The necessary heating is effected by steam circulating through iron or copper pipes, arranged round the walls. Direct heating by ovens is no longer adopted in well-arranged refineries.

Formerly, each mould was placed to drain separately on the floor in a pot, but this inconvenient arrangement has been substituted by placing them on a shelf, perforated with holes of sufficient diameter to receive the points of the moulds, the upper part being supported by a frame. Below the perforated shelf is a zinc-lined funnel, from which the syrup runs off through a pipe into a trough, and is conducted away. The trough is movable, so that, according to the quality of the syrup, it can be connected with special piping communicating with different reservoirs. Each stand holds two or three rows of moulds, so that they can easily be reached, and between each stand is a gangway sufficiently wide for a man to pass. A still better arrangement is for the holes in the shelves to be larger, so that the moulds hang by their broader ends; the head of the moulds and the draining of the syrup can then be more conveniently watched.

The filled moulds remain in the filling room eight to twelve hours, and are then removed to the floor, being raised in a frame by means of a lift. Arrived at the floor, the plug is removed from the head of the mould, and a small hole is bored in the head of the loaf with an awl, to facilitate the running off of the syrup. The temperature of the floor is maintained at 25° to 28°.

The still fluid portion of the sugar, the syrup, drains slowly from the opened mould, and in about twelve hours the upper layer of the sugar appears white and dry. The draining lasts six or seven days longer, during which time 8 to 11 lbs. of green syrup will drain from a large sugar loaf, weighing 33 to 36 lbs. The temperature of the floor is then moderated to 20°, and the liquoring, or displacement of the syrup with pure sugar solution commenced.

By means of a scraper the top layer of sugar is first removed, in order to give to the loaf a smooth base, it having become uneven through the stirring and unequal solidification.

The scraped sugar is then made quite level on the surface, and a further covering of pure ground sugar or white well-clayed colonial sugar given to it: this is beaten close by means of a wooden hammer.

The liquoring or claying is carried out in different ways. The oldest method, and that from which it derived its name, claying, is by means of clay. A paste of clay and water is spread upon the levelled base of the loaf covered with loose sugar; the water gradually drains from the clay, and forms with the loose sugar a saturated solution that passes through the loaf displacing the impure syrup; the pure sugar is left undissolved, the sugar solution being a completely saturated one before it enters the loaf itself.

The clay used must possess a certain capability of taking up water, and be neither too fat nor too lean. In the former case it would retain the water too long and thus protract the operation, whilst in the latter the water would drain away too rapidly. Usually a white pipe clay is used, but the colour is quite immaterial, and a yellow or blue clay answers as well. One thing is essential however; it should not contain any soluble iron salts, pyrites, or soluble organic matters, as these would colour the sugar, the pyrites would become partly oxidised during the claying, and the sugar would be percolated by a syrup containing sulphuric acid and ferric sulphate. The raw clay is first dried, the lumps broken up, suspended in water and washed. The mud is passed through a fine sieve to remove sand; it is then allowed to settle and the supernatant water separated. The paste is again stirred up with fresh water several times, the liquor being separated each time. The prepared paste should form a mud of tolerable consistency; the exact consistency is recognised by an empirical sign. A portion is taken from the mass upon a trowel, and thrown back by a vigorous movement upon the mass, into which it ought not to sink directly but form on it a slight prominence. Enough of this paste is placed on the levelled base of the loaf to form a layer about 1¼ inch thick. As before mentioned, this paste parts with its water, which passes through the sugar, and after a time the clay remains as an almost dry covering on the sugar. Should the syrup not drain off from the sugar sufficiently rapidly, and the clay consequently not remain moist sufficiently long, the operation can be hastened by boring a larger hole in the apex of the loaf. Ordinarily for the medium-sized loaf seven or eight days are required. According to the quality of the product desired the claying is repeated two or three times, the dried layer of clay being removed and replaced by a fresh one. The syrups draining off are known as first, second, and third syrups. With good sugars, as a rule, two layers are sufficient. In order to ascertain this, some moulds are emptied by standing the loaves upon their broad bases, and

knocking them gently upon the floor; the mould separates and it can be lifted off. Should the loaf prove to be unequal in colour, the apex being still yellow, it is a sign that it still retains syrup, and it is subjected to another claying.

About the fourth day after the claying, a knife is passed between the side of the form and the clay in order to prevent adherence; otherwise, since the clay shrinks in drying, it would split and form an imperfect cover. Too sudden changes of temperature and especially draughts are to be avoided, as these also are likely to cause the splitting of the clay. After the green syrup has drained off, the temperature of the floor is moderated in order to dissolve as little sugar as possible.

After the claying is finished, the loaf is laid in a horizontal position and the clay removed by a lathe, which cleans and levels the broad end of the loaf. At the same time the loaf is loosened, but is still left in the mould while a little more syrup runs away. When no more syrup can be removed, in order to distribute any remaining equally through the loaf, it is reversed and allowed to stand on its base still covered with the mould, for twenty-four hours. It is then restored to its original position, and in two or three days again reversed. After twenty-four hours the mould is lifted off, and the loaf is dried, first during a day in the open air, and then in the drying oven, being previously covered with sheets of paper to protect it from dusts and smuts.

Although clay, on account of the gradual and uniform way in which it gives up its water, forms the best cover, it is not now used on account of the time required, and a solution of pure sugar is substituted in its place. This is prepared by making a saturated solution of sugar of the same quality as that required, at the temperature of the room. For this the scrapings and broken loaves are mostly used, or the white colonial sugar. When these latter are used the syrup is first passed through the charcoal filter, to remove any impurities present. In the preparation of the syrup, the quality of the product and the stage of its manufacture have to be considered. It would be wasteful to use the finest syrup for an ordinary product; as it would also be for a fine loaf which had only been drained of the green syrup. For the first liquoring the syrup from the second liquoring of another loaf is used, and for the second liquoring syrup from a third is used, the fresh syrup being used for the third liquoring. Before pouring on the clear syrup the base of the loaf is levelled, sufficient loose sugar being added to make it even. About a quart of syrup is used for each form; after a short time this is absorbed and the operation is repeated till the syrup drains away as clear as water.

For ordinary goods three liquorings are usually sufficient; for the finer five or six are required, the successive liquorings being effected with increasingly clear syrup. The last draining takes the longest time, five or six days being required. The further treatment is then the same as when clay is used.

The methods differ essentially from each other in that when clay is used the syrup is first formed during the operation by the solution of the loose sugar on the base of the loaf, whilst by the other method the syrup is specially prepared. The liquoring presents the advantage that the operation is finished in seven or eight days whilst the claying requires about twenty-four days. Even the shorter method is now abbreviated by the use of apparatus which removes the syrup from the sugar.

One method is to remove the syrup by centrifugal power. The apparatus used for this purpose is shown in fig. 632. The revolving drum is formed of two strong iron cylinders (*a b*). These are perforated by three rows of 12 holes each, the holes in the outer cylinder being of a diameter to fit and support the tops of the forms, and those in the inner cylinder their broad ends. The outer of the two cylinders is about 4 feet in diameter, and the outer case (*c c*) correspondingly wider. The drum being caused to make about 400 revolutions per minute, the syrup is projected from the tops of the loaves, and runs off from the outer case through the spout (D). The draining of the syrup, which by the old method took five or six days, is thus effected in an hour and a half. Larger machines carry 72 moulds and work up 700 or 800 loaves daily. The centrifugal machine however presents no advantage over the extractor apparatus; it requires more driving power, wears out more rapidly, and for an equal capability of production is more expensive in its first cost.

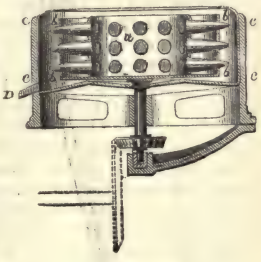


FIG. 632.

The apparatus known as the extractor consists of a system of horizontal iron pipes connected with each other and with a hermetically closed reservoir. Upon these, at intervals corresponding with the breadth of the moulds, are set short vertical pipes, each provided with a tap and supporting a small funnel coated with caoutchouc,

the angle of which corresponds with the shape of the mould. As soon as the syrup ceases to flow off quickly, the moulds are placed with the apex in the funnel of the apparatus, the corresponding tap is opened, and a vacuum set up in the common reservoir and the connected piping by means of an air pump. The air then takes the place of the syrup used; the claying penetrating into the spaces between the crystals and driving the syrup before it into the piping, and thence into the reservoir. This method allows of a much more perfect freeing of the loaves from green syrup with less claying; a small quantity of syrup always remains in this case also, which is dispersed equally by repeated reversals as before described.

The drying oven, or stove, is a space 12 to 16 feet wide, 20 to 28 feet long, and of the same height as the sugar floor. It is surrounded by thick walls, in order to retain the heat and prevent variations in the temperature. The heating is effected by steam pipes, and the inlet of fresh air and the outlet of damp air is regulated by means of openings in the floor and at the top. The frames for supporting the loaves of sugar are so arranged as to admit the greatest possible number of loaves into the oven at one time. Each stove usually accommodates from 2,000 to 4,000 loaves, and the drying must be very carefully watched. At first the temperature is raised only slightly above that of the room from which the loaves have been removed, and the heat is afterwards gradually increased. Were the heat to be applied too rapidly, the relatively large quantity of syrup still present would become saturated with sugar at the higher temperature, and might melt the loaf. The stronger heat should be first applied when the greater part of the water of the syrup has evaporated, and only a little syrup is left. Finally, the temperature is raised to 50° or 60°, to remove the last traces of water from the sugar.

The temperature is regulated by the opening or closing of the steam cocks. The condition of the sugar is ascertained by entering the oven, and inspecting the separate loaves. The drying is completed when the loaves give a clear clang upon being struck. During the drying, all sudden variations of temperature have to be avoided; the current of air caused by the rapid opening of a door might cause the splitting of a loaf. For the same reason the cooling of the oven should be gradual, the door being allowed to stand open at last, in order to allow the temperature of the oven to become assimilated to that of the sugar floor.

The sugar now needs a little cleaning externally, spots of dirt being removed with a scraper, and dust with a brush. The finished loaf is then encased in paper, and is ready for the market.

After Products of Sugar Refining.—The different syrups of the refinery are collectively still capable of crystallisation, and yield upon further boiling products which, although not such fine sugar, are still almost white; these are brought into commerce under the names of crystallised and flour sugar. Not only the syrups are thus worked up, but the ordinary raw sugar, the droppings and the sweepings of the sugar floor, etc. These are placed with some added water in the clarifying pan, boiled with inferior charcoal, and filtered. The boiling of old syrups must be carefully conducted, as generally they are in slight fermentation; they therefore contain carbonic dioxide, which is driven off by the heat, and may easily cause a frothing over of the hot syrup. In such case the froth is broken by carefully spirting water into it. The improved machinery yields syrups that are not so old; the stronger fermentation therefore does not take place, and the frothing over is avoided.

According to the quality which it is desired to give to the after products, the filtration is more or less carefully carried out. For this purpose the filters are used through which the syrup has already passed in the first refining. The finer syrups are boiled to granulation, the inferior are boiled blank. The moulds for the after products are larger than for the refined; the crystallisation takes a longer time, and the draining of the more impure syrup takes place more slowly. The sugar is again well clayed, in order to have the loaf as equal in colour as possible. The loaves are sometimes yellow or brown at the top. These tops are usually broken off, and the whiter remaining portion broken up into large pieces or lumps. The more coloured loaves are ground after drying, and the powder sold as flour sugar. With the better secondary products, the artifice is frequently practised of boiling them with a little ultramarine, by which the sugar acquires a faint blue colour that covers and is more acceptable than its natural yellow tinge.

The last syrup collected in a large receptacle still yields a further crystallisation, which, after being submitted to the centrifugal action, is used as raw sugar, or after liquoring in the centrifugal machine is mixed with flour sugar.

The molasses finally remaining in the refinery is always far superior to that of the sugar manufactory. It can be directly consumed, or is sold for making sweet pastry; it is sometimes added to beer worts.

Description of a large Paris Refinery.—Fig. 633 shows the general arrangements

for dissolving, raising, clarifying, and filtering the syrup. The pan (A) is used for melting the sugar; it is 10 feet in diameter and 10 feet deep. It stands on the ground floor of the building. The sloping bank (B) is used for the raising of the raw sugar to the pan. Into the pan is first brought about 380 gallons of water, or a corresponding quantity of thin syrup obtained by washing the filters. During the throwing in of the sugar steam is let into the spiral to raise the temperature of the liquor to 50°, at the same time the stirrer (D) is set in motion by the driving wheel

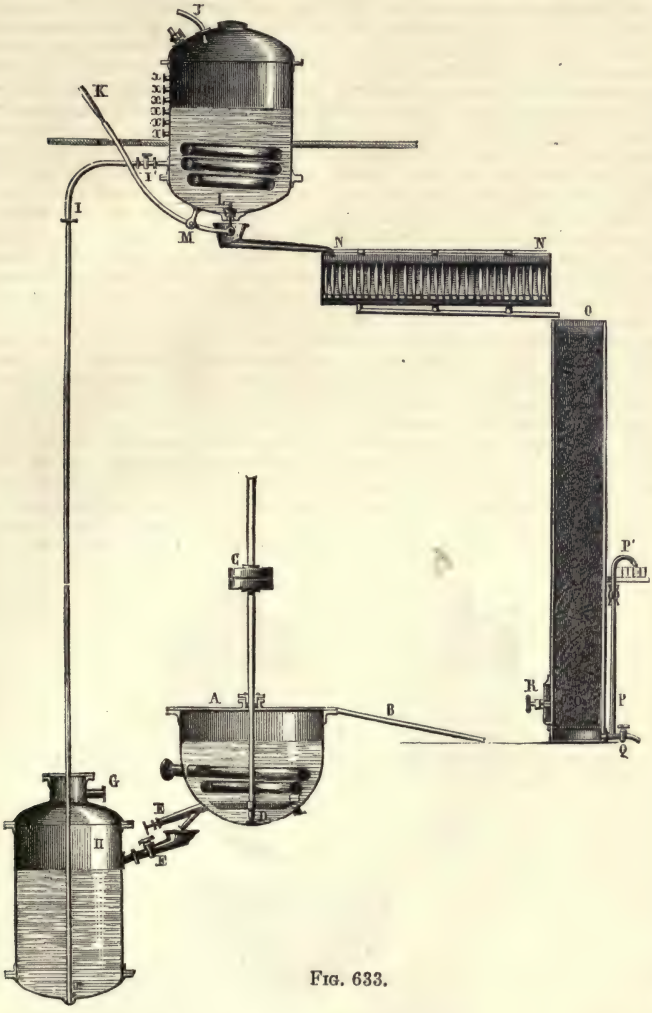


FIG. 633.

(C). When about 5 tons of sugar have been thrown in and melted, if the syrup has a slightly acid reaction enough lime is added to render it neutral or faintly alkaline, and afterwards about 2 cwts. of ground animal charcoal and 12 gallons of blood. After being thoroughly mixed by the stirrer, the valve (E) is opened, and the mixture runs through the funnel, provided with a tap (F), into the monte-jus (H), until it is three-fourths full. The tap (F) being then closed, steam under a pressure of five atmospheres is admitted through the pipe (G). The pressure of the steam and of the expansion of the air resulting from the heat drives the mixture through the pipes (I I) into the clarifying pan (B), placed at a height of 50 feet. This is entirely closed and

provided with a condenser. When it is three parts filled with a mixture of syrup, charcoal, and blood, the cock of a steam pipe (J), terminating in a rose in the interior of the boiling space, and just over the surface of the mixture, is opened, and steam admitted until all the air has been expelled through the open air cock and the space is completely filled; the steam and air cocks are then closed. By the condensation of the steam a partial vacuum is rapidly produced over the mixture, which is maintained by the action of the condenser. In other factories the vacuum is produced by an air pump; steam is then admitted into the spiral, and the mixture heated to vigorous ebullition, in order to effect the most intimate mixture possible of the ingredients. The air cock is then opened, destroying the vacuum, and the temperature rapidly raised to the boiling point under ordinary pressure, which with this concentrated solution is 105°. The temperature is taken with a thermometer, the bulb of which is in the liquor, whilst the scale is outside the apparatus. A manometer shows the internal pressure; the progress in the boiler can be watched through lunettes (x x x), which are lighted by a lamp shining through a similar lunette on the opposite side. As soon as the mixture boils, the valve (L) is opened by pressure upon the lever (K), the fulcrum of which is at M; the mixture then runs out into the preliminary filter (N). This is arranged for filtration from outside to inside as described at p. 862. The clarified syrup runs from thence through a trough on to the charcoal filter.

The melting of the sugar in the pan (A) takes about 50 minutes, so that in twenty-four hours about twenty-five operations can be effected, equal to about 130 tons of sugar. Each preliminary filter is 7 feet 4 inches long, 5 feet 10 inches wide, and 4 feet 10 inches deep. Twelve of these filters stand side by side, and are used simultaneously.

The charcoal filter (O), 4 feet in diameter and about 36 feet in height, is provided with a manhole (R), an emptying tap (Q), and an ascending pipe (P), 13 feet high. Each filter contains nearly 300 bushels of animal charcoal, and 25 filters are used. Every twenty-four hours four of these filters are emptied, so that nearly 1,200 bushels of charcoal require to be revivified daily.

The filtered syrup, the whiteness of which is carefully watched, is conducted into the reservoir of the vacuum apparatus. The boiling apparatus (A, fig. 634) is arranged as shown in figs. 623 and 624, and described on p. 850. It is connected above at B with a condenser and an air pump. The boiling is conducted so as to obtain the crystals larger or smaller according to the product required. It is quickly accomplished, as the syrup comes into the apparatus with a previous concentration of

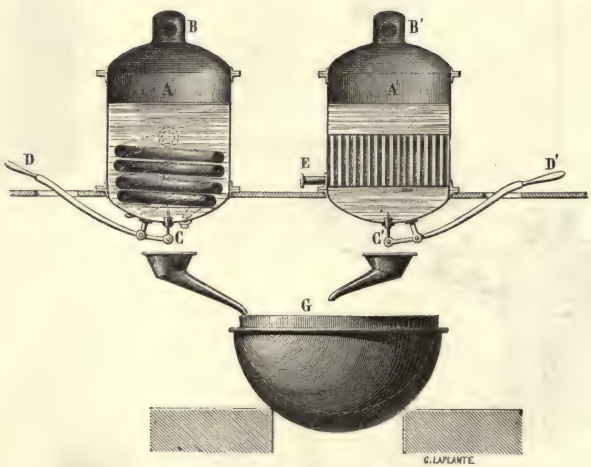


FIG. 634.

55° to 58° S. (sp. gr. 1·245). The apparatus is 10 feet in diameter and 16 feet high, and its capacity corresponds to the syrupy mixture containing 13 tons of sugar. As ten or twelve operations can be carried out daily, one apparatus is sufficient for the entire quantity. The steam spirals of the apparatus have a heating surface of about 320 square feet; the steam enters under a pressure of five atmospheres, or at a temperature of about 150°.

After sufficient concentration the emptying is effected by means of the valve (C),

which is opened inwards by pressure on the lever (D). The syrup then flows into double-bottomed heaters (G), each of which has a diameter of 10 feet and a depth of 6 feet. The subsequent operation in the filling room and the sugar floor is carried out as before described.

The apparatus for drawing off the syrup consists of three horizontal pipes, upon which 1,500 moulds find room simultaneously; the drawing off of the syrup lasts 1½ hours. The air pump of this apparatus is worked by a 70 horse power engine.

Each floor has its stove, and each stove holds in three rows, standing one above another, 1,500 to 3,000 loaves weighing 22 lbs. to 26 lbs. each. The heating is effected by waste steam passing through four pipes, 6 to 8 inches in diameter, arranged one above another on one of the walls.

The boiling of the clayed syrups is carried out in a special vacuum apparatus (A', fig. 634), 8½ feet in diameter and about 17 feet high This is heated like Robert's apparatus, by a system of 2¼-in. pipes, 40 inches long, fitted between the two bottoms, and having a heating surface of nearly 1,000 square feet. The steam enters at the side through a pipe (E), circulates between the pipes, and passes then with the condensation water into the steam chest. These syrups are boiled to thread proof, consequently blank boiled; the granulation is carried out in coolers standing by the side of the heater (G).

After the first granules form the crystallisation is finished in from twenty-four to forty-eight hours, in a cast-iron vessel holding about 11 gallons. The syrup from this product is boiled in the same apparatus, and then crystallised in an iron vessel of upwards of 100 gallons capacity, the crystallisation lasting five or six days. The third, fourth, and fifth crystallisations yield flour, which is swung in the centrifugal apparatus and then liquored. The crystallisations take place in vessels of constantly increasing size, respectively containing 200, 400, or 800 gallons; the time, likewise, required for the crystallisation continues to increase, the last crystallisation requiring four to eight months, during which the vessel is kept at a temperature of 35° to 40°. The syrup of the last crystallisation constitutes molasses, which still contains 50 to 55 per cent. of crystallisable sugar.

The proceeds of the final crystallisations are well drained and methodically liquored in the centrifugal apparatus, using purer syrup at each liquoring, and finally a jet of steam is allowed to play upon the rotating mass in the drum from a finely perforated pipe at a distance of 2 or 3 inches. The steam condenses in the sugar and forms syrup which rapidly permeates the sugar loaf, carrying before it the impurer portion.

All the unclayed sugars undergo the same purification. Sugar that has been already clayed, and is suitable, is treated once with steam, and then, after solution and filtration through charcoal, used for clear liquor. Sugar, of which the grain is too fine to bring it into the centrifugal apparatus, is first granulated, by melting, clarifying, filtering, and allowing it to crystallise in large vessels; it is then swung. It will be seen that in this manufactory only sugars almost free from syrup are used; the inferior cane sugars are first recrystallised, in order to obtain the purest possible material for the refinery. The advantage is that the crystallisations are easily effected, and the refinery syrups can be worked up almost to the last drop. For the claying there are forty centrifugal apparatus 32 inches in diameter, each of which is filled with about 100 lbs. of syrup; the rotation required is about 1,200 revolutions per minute.

Manufacture of Sugar Candy.—The name of candy is applied to well-formed crystals of sugars of different colours. The principal shades met with in commerce are white, straw-coloured, and brown. The consumption of candy is comparatively limited and localised in certain districts; thus East Friesland, Holland, and Belgium consume large quantities of candy, whilst in other countries its use is almost unknown. The manufacture is carried on either in refineries or in special candy-boiling houses.

In the preparation of white candy, the finer refined or quite white tropical sugars are used; clayed beet-root sugar cannot be used for the purpose, as the large crystals always contain some enclosed syrup, which would communicate to the candy an after-taste and smell. This after-taste makes such candy perfectly unfit for the manufacture of sparkling wines, in which it finds its principal use, whilst the peculiar aroma of the colonial sugar is a desideratum. Through the great purity of the raw material the crystallisation may easily take place too rapidly, and instead of large crystals, small indefinitely formed ones are obtained. According to Payen, this may be avoided by adding to the syrup, when placed for crystallisation, 1 part in 1,000 of tartaric acid.

The straw-coloured candy is prepared either from beet sugar, or from a mixture of Havannah and Indian sugars. The brown is especially prepared from Brazil sugar.

The first operations of the candy manufacture are similar to those of refining.

The sugar is melted in water in a pan (A, fig. 635), and clarified by the addition of animal charcoal and albumin; the syrup is then passed through the preliminary filter (B), and is brought to the right degree of decolorisation in the charcoal filter (C). From

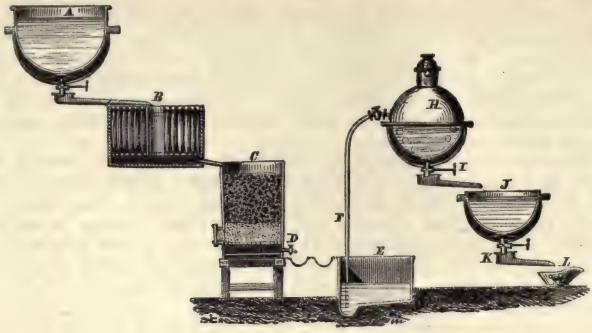


Fig. 635.

thence it flows through a tap (D) along a trough into the reservoir (E), from which it is drawn through the pipe (F) into the vacuum pan (H). In the place of the vacuum pan, there is still found in many candy factories copper swinging pans heated over an open fire. When the vacuum pan is used, the evaporation is only carried on to slight stringiness, and then the syrup is allowed to run off through the valve (I) into the heater (J), where the boiling is finished. The evaporation is conducted differently according to the quality of the syrup. With the most easily crystallising white candy, it is carried farther than with the darker sorts. Generally the finish of the evaporation is recognised by empirical tests, such as the bubbles, or the boiling mass is tested with an areometer. With white candy the evaporation should be carried to a specific gravity of 1·357, the straw-coloured to 1·363, and the brown to 1·369.

As soon as this stage is reached, the hot mass is removed by means of the filling bowl (L, fig. 636), into the crystallising vessels or candy pots, which are erected in the candy room, a strongly heated space, similar to the sugar stoves (figs. 636 and 637). The candy pots are round copper bowls, with flat bottoms and sloping sides. In the sides are fine holes, through which, before the filling, fine threads are drawn for the crystals to form upon. After the introduction of the threads, the holes are plastered over with paper on the outside. The candy rooms differ from the sugar stores by being ventilated as little as possible, consequently no steam draught is used. The frames upon which the pots stand are separated about 14 or 16 inches from each other. By means of an externally heated oven, or better still by steam pipes, a temperature of 60° is maintained for seventy-two to seventy-six hours; then the heating is stopped, and the room is kept closed for nine days. By the twelfth day the temperature has sunk to 35° to 38°. In all cases, sudden variations of temperature, shaking of the vessels, or draughts, are avoided, as causing a proportionate irregularity in the cry

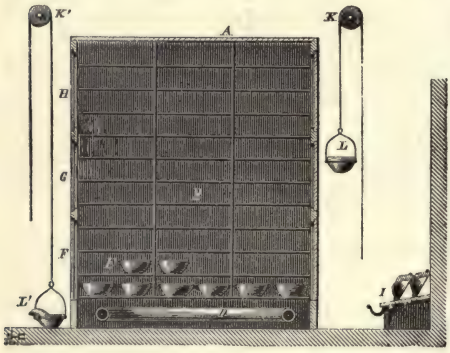


Fig. 636.

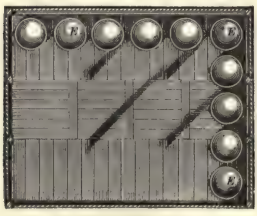


Fig. 637.

stals. The temperature is observed upon a thermometer placed inside the room against a window in the door.

In medium-sized vessels, the crystallisation proceeds far enough by the twelfth day; with small vessels and white syrup, the crystallisation is ended earlier; with the grosser and more impure syrups, especially if very large crystals are required, it lasts longer. The crystallising vessel is then taken out, a hole broken in the crystalline crust that forms on the surface, and the greater part of the syrup poured off, and the rest left to drain by placing the bowl in an inclined position over a trough. The last adhering syrup is washed off with lukewarm water and this is again left to drain over a trough. During the draining, the surface of the candy becomes dried, and the threads are then cut from the outside and the candy lifted from the pots. Lastly, it is dried at a temperature of 36° for twenty-four hours, and, either whole or broken into pieces, is sent to market.

In the factory from which the foregoing description is taken there are six candy rooms side by side. Each has three doors (F G H) placed one over another, corresponding with as many stages fitted with frames. Opposite the doors, pullies (K K′) are placed for the convenient raising of the filling bowl (L′) and the removal of the crystallising pots (L). Each oven is 18½ feet high, 13 feet long, and 10 feet wide, and contains ten stages one over another, each supporting thirty pots, so that the entire room holds 300 pots. The pots are 24 inches in diameter and 13 inches deep, and hold when full 110 lbs. of syrup, which yields 55 lbs. of candy. The emptying of the oven is effected through doors at the back of the oven.

The syrup drained from candy is boiled for loaf sugar.

SACCHARIMETRY.—The determination of the amounts of sugar in various materials is effected by one or other of the following methods:—

1. Chemical methods, based upon the known capability of some kinds of sugar to reduce metallic oxides either to a lower state of oxidation or to the metallic state.

2. Areometric methods, based upon the observed relation between the specific gravity of a sugar solution and the amount of sugar it contains.

3. Optical methods, based upon the power of cane sugar to turn the plane of polarisation of a ray of light to a certain extent to the left hand.

Chemical Methods.—Of these, the first to be mentioned is Fehling's. It is founded on the fact that glucose, or the mixture of grape and fruit sugar obtained when a solution of cane sugar is boiled with a little hydrochloric, sulphuric, or oxalic acid, reduces cupric oxide in alkaline solution to cuprous oxide.

Pure cane sugar has no such reducing action. Essentially, the method has been described before on p. 804. 1 gram of the substance to be examined, a sample of cane sugar, for instance, is dissolved in about 50 c.c. of water, in a flask holding exactly 100 c.c. up to a mark in the neck, a few drops of a concentrated solution of oxalic acid are added, and the solution boiled in order to convert the cane sugar into the mixture of two kinds of sugar known as inverted sugar. After the liquid is cool the free acid is neutralised with sodium carbonate, the solution diluted to exactly 100 c.c., and titrated according to the method described on p. 804. An amount of grape sugar is thus found corresponding to the amount of cane sugar originally present. As the quantities of grape sugar and cane sugar concerned in this reaction are in the proportion of 360 to 342, the quantity of cane sugar corresponding to the grape sugar is easily calculated.

The same method admits of the estimation of the two kinds of sugar—cane sugar and grape sugar—when they occur together. The solution can be titrated at once, to determine the amount of grape sugar present, and again after boiling with acid. The difference between the amounts of grape sugar found in the two operations represents the amount of cane sugar.

This method is not without disadvantage. It is especially difficult to determine the exact point at which all the cupric oxide is reduced, and not to add sugar in excess. In proportion as the greater portion of the copper is reduced, the previously intensely blue liquid loses its colour, until at last it is very doubtful whether it has still a blue shade or not. In effecting the perfect reduction of the cupric oxide, it becomes uncertain whether or not too much sugar has been added. In order to avoid this uncertainty, an excess of copper solution is used, and the quantity of oxide reduced by it is estimated. 60 c.c. of Fehling's solution of the strength previously given is diluted with two or three times its volume of water, heated to boiling, and so much of the solution to be examined added as shall contain not more than 0·250 gram of sugar. As the quantity of copper solution would require 0·300 gram of sugar to reduce it perfectly, an excess remains. After a short boiling the liquor is allowed to stand; the heavy intensely red coloured precipitate of cuprous oxide settles rapidly to the bottom, and the clear blue supernatant liquor can be decanted off. Boiling

water is then poured over the precipitate, and it is again left to settle; afterwards it is thrown upon a small filter and washed as quickly as possible. The filter is then dried, and the precipitate, after the combustion of the filter, is kept at a red heat for some time in contact with air to convert the cuprous oxide into cupric oxide. To ensure that no trace of cuprous oxide remains, it is moistened with a drop of nitric acid, carefully dried, and again brought to a red heat. From the weight of cupric oxide found, the amount of sugar can then be calculated.

One molecule of cane sugar, or 342 parts by weight, after being changed into inverted sugar, reduces ten molecules, or 794 parts by weight of cupric oxide; the same quantity of cupric oxide is reduced by two molecules, or 360 parts by weight of grape sugar. But as the cupric oxide found is produced from the reduced cuprous oxide, the statement is:

$$x : 1 = 342 : 794$$
$$x : 1 = 360 : 794$$

the unit of weight of cupric oxide corresponding to:

0·4307 cane sugar, and
0·4534 grape sugar (inverted sugar).

A large number of estimations carried out by Scheibler with chemically pure sugar showed that the sugar quantities calculated from the cupric oxide obtained are a little too high, and that a more exact result is arrived at when the cupric oxide obtained is multiplied by:

0·43 for cane sugar, and by
0·45 for invert sugar.

Other methods have been recommended for the estimation of the precipitated cuprous oxide. One is to dissolve the cuprous oxide in hydrochloric acid, with the addition of sodium chloride, and to convert the cuprous chloride thus formed into cupric chloride, with a titrated solution of potassium permanganate. Or the cuprous chloride may be treated with ferric chloride, a corresponding quantity of ferric chloride being converted into ferrous chloride; the ferrous chloride can then be estimated with potassium permanganate or chromate. These methods do not present any advantage over the method above described.

Another easily worked method is based upon the fact that invert sugar completely reduces mercury from an alkaline solution of mercuric cyanide; according to the observations of K. Knapp, 100 parts of grape sugar being required to reduce 400 parts of mercuric cyanide. A titrated solution is used consisting of 10 grams of pure crystallised mercuric cyanide dissolved with 100 c.c. of solution of caustic soda (sp. gr. 1·145), to make 1,000 c.c. 40 c.c. of this liquor, representing 0·100 gram of grape sugar, is boiled and then allowed to act upon the sugar solution until the whole of the mercury is precipitated to the bottom of the vessel in small globules. A drop of the boiling liquid placed on a fine filter paper, and held over a vessel containing concentrated ammonium sulphide, will undergo a brown coloration, owing to the formation of mercuric sulphide, so long as any mercuric cyanide remains unchanged; but the moistened spot remains colourless when mercury is no longer in solution. In estimating by this method, the process followed is the same as described on p. 804. A gram of sugar is dissolved—in the case of cane sugar, after being inverted by the addition of acid and heating—and made up to 100 c.c. In the first estimation, the point is approximately sought at which to stop the addition of sugar, and this is determined exactly by a repetition.

The *areometric method* of determining the amount of sugar gives exact results only with solutions of pure sugar, but when other substances are present they affect the specific gravity of the liquid. Nevertheless this method is very generally used for some purposes. The accompanying table gives the results of Gerlach, which correspond very closely with those of other observers.

When the specific gravity has been taken the sugar contents can be easily ascertained from this table. But, in order to avoid this trouble also, Brix and others have constructed special areometers, or saccharometers, upon the scales of which the percentage of sugar is directly indicated. Of the various saccharometers, that of Brix is the most generally used. In using these instruments it must be borne in mind that, since all liquids become lighter by expansion, the same liquid, for instance, will give a different saccharometer figure at a temperature of 10° to what it does at 15°. It is therefore necessary to make all observations at the particular temperature for which the instrument is constructed, usually 17·5° C.; colder solutions have therefore to be heated and warmer solutions cooled to this point. On the other hand, the indications of the saccharometer can be reduced by means of the table to the corresponding specific gravities.

The saccharometer used in Great Britain is that constructed by Bate. The stem bears a scale of divisions numbered downwards to 30°. Each of these divisions indicates a one-thousandth part of the specific gravity of water.

Sugar. Contents of solution. Weight per cent.	Specific gravity at 17·5°	Sugar. Contents of solution. Weight per cent.	Specific gravity at 17·5°	Sugar. Contents of solution. Weight per cent.	Specific gravity at 17·5°
1	1·003880	26	1·110646	51	1·238293
2	1·007788	27	1·115330	52	1·243877
3	1·011725	28	1·120048	53	1·249500
4	1·015691	29	1·124800	54	1·255161
5	0·019686	30	1·129586	55	1·260861
6	1·023710	31	1·134406	56	1·266600
7	1·027765	32	1·139261	57	1·272379
8	1·031848	33	1·144150	58	1·278197
9	1·035961	34	1·149073	59	1·284054
10	1·040104	35	1·154032	60	1·289952
11	1·044278	36	1·159026	61	1·295890
12	1·048482	37	1·164056	62	1·301868
13	1·052716	38	1·169121	63	1·307887
14	1·056982	39	1·174222	64	1·313946
15	1·061278	40	1·179358	65	1·320046
16	1·065606	41	1·184531	66	1·326188
17	1·069965	42	1·189740	67	1·332370
18	1·074356	43	1·194986	68	1·338594
19	1·078779	44	1·200269	69	1·344860
20	1·083234	45	1·205289	70	1·351168
21	1·087721	46	1·210945	71	1·357518
22	1·092240	47	1·216339	72	1·363910
23	1·096792	48	1·221771	73	1·370345
24	1·101377	49	1·227241	74	1·376822
25	1·105995	50	1·232748	75	1·383342

The optical method of ascertaining the amount of sugar in different solutions is based upon the fact that a fixed quantity of sugar in solution rotates the rays of a beam of polarised light exposed to its action to a known extent right or left.

The apparatus of Mitscherlich consists of two Nicol calc spar prisms, which in the normal arrangement of the instrument are so placed opposite to one another that the rays of light passing through the first prism are completely absorbed by the second. If a liquid capable of deviating the plane of the beam of light be brought between the two prisms, the absorption by light of the second prism no longer takes place; it appears much more illuminated, and, according to the extent of the deviation, of a red, yellow, green, blue, or violet colour. In order to measure the amount of deviation, the second prism is rotated until the field of sight appears half blue and half violet coloured, the distance being shown by a pointer connected with the second prism and moving round a circle divided into 360 parts.

A column of liquid 200 mm. long, consisting of sugar solution containing exactly 30 grams of chemically pure cane sugar in 100 c.c., rotates the beam of polarised light exactly 40°. With columns of liquid of the same length, but containing an unknown amount of sugar in solution, each degree which the second prism has to be rotated indicates 0·75 gram of sugar in each 100 c.c.

Soleil's apparatus has the Nicol prisms the same as that of Mitscherlich, but between them is inserted a further arrangement, which facilitates the observation considerably. The ray of light polarised by its passage through the first prism passes then through a plate of quartz cut perpendicularly to the axis of the crystal. It is divided through the middle of the field of vision, so as to form a disc consisting of two halves, one half rotating to the right and the other half to the left. With a thickness of one-eighth of an inch, these plates appear when viewed through the second Nicol prism of one colour, quite faint and between green and red. The least rotation of the polarised ray at once produces a change of colour, towards green on the one side and red on the other. The ray of light then passes through another quartz plate cut perpendicularly to its axis, and then through two wedge-shaped quartz plates, having both equal but opposite rotating powers like the plates above mentioned. The two wedge-shaped plates with their settings are connected with mechanism by

which they can be pushed over one another so as to form one plate of variable thickness. On the frame of one of these plates is a scale and on the other an index. The zero of the scale is so placed that it coincides with the index when the thickness of the two wedges equal the thickness of the plate p''. In this position the effects of both are completely neutralised, and on looking through the second prism the above-mentioned faint colour is again seen, whilst in any other position of the wedge-shaped plates the red and green colours appear. The further divisions of the scale are so made that at the point 100 the thickness of the plate formed by shifting the two wedges is exactly 1 millimeter, or one twenty-fifth of an inch. Finally the ray of light passes to the second prism.

The apparatus is represented by figs. 638 and 639. Between the tubular ends T T′ and T″ T‴ is a space to receive the tube containing the liquid to be examined. The

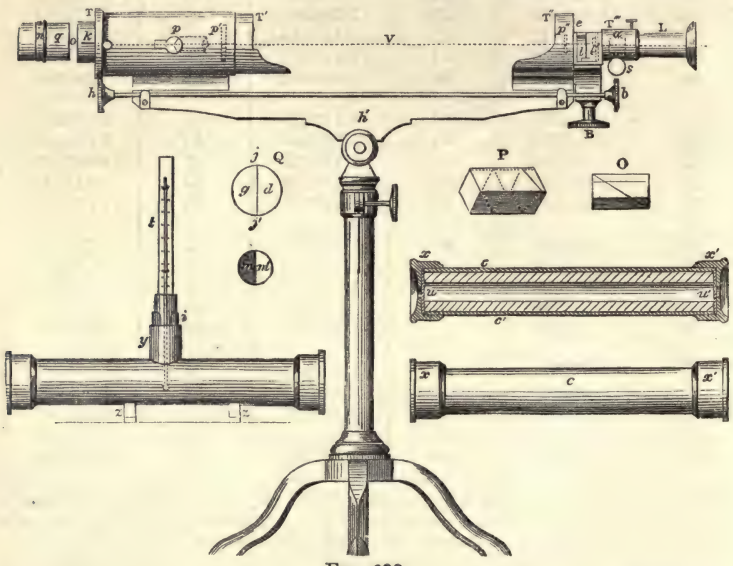


FIG. 638.

Nicol prism is placed at q and the quartz plates at p and p . The quartz wedges (l and l') are represented on a larger scale in fig. 639. They are made to slide backwards and forwards by turning the milled head (B′, fig. 638).

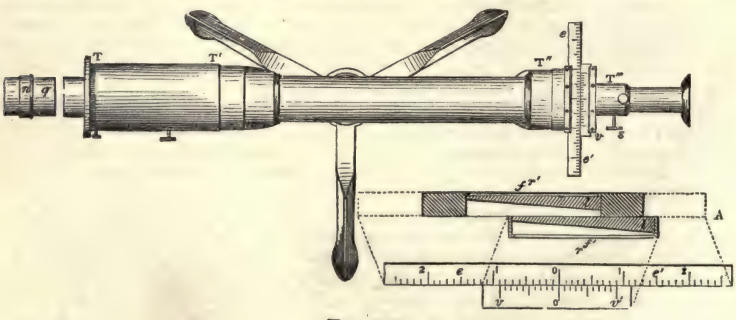


FIG. 639.

When a sugar solution is brought between the two quartz plates p and p'', its rotative power enhances the rotation of the polarised ray by the one half of the double plate p', and weakens the action of the other half. Both halves thus acquire a different colour; the uniformity of colour is again restored when the wedge-shaped quartz plates are shifted, until the thickness of the plate formed corresponds with the rotative power of the interposed sugar solution.

The rotating power of a quartz plate $\frac{1}{25}$ in. or 1 mm. in thickness equals that of a column of liquid 200 mm. long, containing 16·350 grams of chemically pure cane sugar in each 100 c.c. If, therefore, a tube, exactly 200 mm. long, filled with sugar solution of unknown strength, be placed between the quartz plates p' and p'', and the two wedge-shaped quartz plates be shifted until the uniform colour is again produced on both sides, each degree of the scale will correspond to a sugar contents of 0·1635 gram in each 100 c.c. of the solution.

Ventzke's apparatus is a modification of Soleil's. It is so arranged that a layer of sugar solution 200 mm. deep, of sp. gr. 1·100, requires exactly 100° shifting of the scale. Such a solution contains in 100 c.c. 26·048 grams of sugar; each degree of the scale corresponds therefore to 0·26048 gram of fine sugar in 100 c.c. of the solution.

In using the polarisation apparatus its correctness has first to be ascertained, as regards the placing of the zero point, the thickness of the quartz wedges, the division of the scale, and the length of the observation tube. In order to ensure a correct placing of the zero point, an empty tube, or one filled with pure water, is placed between the two prisms of Mitscherlich's apparatus, or between the two quartzes of a Soleil or Ventzke's apparatus; the light of a clear burning lamp is allowed to fall on the apparatus, and an observation is made after the index has been placed exactly upon the zero point. In Mitscherlich's apparatus the light should be absorbed and the field of vision become darkened. In the other two forms of apparatus, upon looking through the eye-piece in front of the second prism, a very small bright disk, divided through the middle by a sharp streak, and uniformly coloured on both sides, should be observed. In this case the apparatus is in order in respect to its zero point; but if the disk is not darkened in the Mitscherlich's apparatus the prism is turned until complete obscuration takes place, and then the index is placed exactly over the zero point. In the Soleil and Ventzke's apparatus the disk may appear uniformly coloured, but of an intensely red or blue colour. This is induced by the position of a third prism, not previously mentioned in this description, which in Soleil's apparatus is situated immediately in front of the eyeglass, and in Ventzke's before the first prism. This prism is therefore arranged so that the intense colour disappears and the illuminated field is as free from colour as possible. If both halves of the disk are then uniformly coloured the zero point is correct; but if one half has a green tint and the other a red tint the quartz wedges are to be shifted until perfect uniformity of colour is produced. If the instrument is furnished with an arrangement for the adjustment of the quartz wedges they should be arranged so that the index coincides exactly with the zero point. If this cannot be done the correct point is noted, and a corresponding correction is to be made after the observations. The correct position of the zero point should be ascertained previous to each use of the instrument. In order to test the apparatus further a solution of pure cane sugar is prepared by dissolving 163·5 grams in water and diluting to exactly one litre. For this purpose pure white sugar candy is finely powdered, and, after being washed with some ice-cold water, drained, and washed with very strong alcohol, the powder is pressed between filtering paper, dried in the air and afterwards at 100°. When this solution is put into a tube 200 mm. long, the quartz plates require to be shifted until the index stands exactly over 100°, in order to produce uniformity of colour. Of the same solution, 10, 20, 30, 40, 50, 60, 70, 80, and 90 c.c. are mixed with 90, 80, 70, 60, 50, 40, 30, 20, and 10 c.c. of water respectively, and these solutions being observed in the apparatus, always in a column 200 mm. long, in order to produce with them uniformity of colour the index should require to stand at 10°, 20°, 30°, etc. Mitscherlich's apparatus is tested in a similar manner, but of course using a different amount of sugar. If it should happen that the figures do not correspond, but that the differences are proportional; if, for instance, with the concentrated solution the index stands at 102° instead of at 100°, when diluted with half water at 51°, and when tenfold diluted at 10°·2, this would be an indication that the quartz wedges are somewhat too thin, but quite evenly ground, or that the tube is a little too long. A correction would then be made that would always show the value of a single degree:—

$$102 : 16{\cdot}35 = 1 : x;\ x = 0{\cdot}1603.$$

Each degree of the scale would consequently in this case represent 0·1603 gram in 100 c.c. of solution. If on the other hand the variation is not proportional, this may be the result of the scale being incorrectly divided, or the quartz wedges not being equally ground; either of these conditions renders the instrument perfectly worthless.

Some modifications of the operation have to be made according as crystallised sugar, intermediate products, or crude products have to be examined.

(*a.*) Crystallised sugar.—In this case the cane sugar, moisture, ash, and glucose have to be estimated. In most kinds of continental sugar there is either no glucose, or it is present in such small traces as not to be worth notice, and this circumstance greatly simplifies the experiment. For the estimation of the amount of

sugar, when Soleil's apparatus is used, 16·35 grams of a well-mixed sample are thoroughly dissolved first in 50 c.c. of water, and then sufficient added to measure exactly 100 c.c., and filtered. The filtration is absolutely necessary, as the smallest quantity of suspended substance in the liquid renders the observation very difficult. Refined white crystallised cane sugar yields a colourless solution, but the raw sugar gives a coloured liquid, the colour of which can in most cases be removed by the addition of a few drops of basic lead acetate solution before the dilution. Many kinds of sugar however that are thus decolorised do not give a clear solution and pass turbid through the filter. Such solutions, according to Scheibler, can be cleared by the addition of a small quantity of aluminum hydrate suspended in water. It is necessary that the solution should be quite clear after filtration. The observation tube, 200 mm. long, carefully purified and dried, is then filled with the solution, and the observation made as previously described. The estimation of sugar in molasses is made in a similar way, but the precipitation of the foreign matters in it requires a larger addition of lead acetate.

The amount of moisture is determined by drying a weighed quantity of the sugar in a small shallow dish until it no longer loses weight. The amount of ash is ascertained by incineration, but the sugar carbon does not burn readily, and is so enveloped in the fused salts, that either some of the salt is driven off by the heat or some of the carbon remains unburnt. This difficulty is overcome by a method introduced by Scheibler. 1 to 2 grams of the sugar are weighed in a small shallow dish, moistened with rather concentrated sulphuric acid, and at first carefully heated. After the greater part of the organic matter has been destroyed the dish is placed in a small muffle, formed of two sheets of platinum bent together, and heated to redness, when the remainder of the carbon is easily burnt. The white ash consists of sulphates, and the half of its weight is taken as the amount of ash. This method is allowable with crystallised sugar, where the amount of ash is always small; in the examination of molasses, beet juice, etc., another method has to be adopted.

When glucose and cane sugar are associated together, the polarisation apparatus can be used, but the chemical method is then preferable. A weighed quantity dissolved in water is mixed with cupric oxide solution, and heated for ten minutes in a water bath at a temperature of 75°; all the glucose is thus decomposed. A second quantity is treated as described on p. 871. The first experiment gives the quantity of glucose present; the second the quantity of inverted sugar originating from the cane sugar plus the glucose. The difference represents the amount of inverted sugar formed from the cane sugar present.

(*b.*) Molasses.—In order to estimate the amount of water present in molasses, it is advisable to distribute it over a large surface by mixing it with some anhydrous substance, because otherwise, in drying, it forms a dense layer from which the complete removal of the water is very difficult. A crucible is half filled with sand and heated to redness; then allowed to cool completely, and weighed. A cavity is made in the sand with a platinum spoon, into which a small quantity of molasses is poured, and it is again weighed. Upon heating, the molasses is liquefied and permeates the sand, and can then be easily dried at a temperature of 100°.

The sugar is estimated as before described. On account of the large quantity of foreign constituents a considerable precipitate is produced on the addition of lead acetate. As the volume of this precipitate would influence the volume of the liquid to be examined it is better to dilute the solution to a greater degree. 16 grams of molasses are dissolved in about 200 c.c. of water in a flask of 250 c.c. capacity; lead acetate is then added and the liquor brought to the correct volume. If the filtered solution is not sufficiently colourless for polarisation, a second sample is prepared with a larger addition of lead acetate. When this does not give a satisfactory result the liquid may be shaken with some animal charcoal previously dried at 100°. But the use of the charcoal is to be avoided as much as possible, because it absorbs a portion of the sugar as well as the colouring matters.

As molasses may contain, besides sugar, other bodies influencing polarisation, the estimation should be controlled by a second experiment made according to the chemical method. In estimating the ash about 10 grams of molasses are heated, at first very gently, in a platinum dish of at least 200 grams capacity. Gradually, as it ceases to froth strongly, the heat is increased until finally the entire mass is carbonised and no more empyreumatic vapours are given off. The voluminous charcoal is broken up, boiled with water, thrown upon a filter, and washed until the washings cease to give an alkaline reaction. The charcoal is then dried, and with the filter incinerated at a bright red heat. The aqueous solution is poured over the resulting white ash, evaporated to dryness, and heated until the whole of the water is driven off. If the charcoal were incinerated without lixiviation, the potash and sodium salts might be volatilised at the high temperature required, and a considerable proportion of the ash constituents lost; moreover the ash would not be obtained free from carbon.

(*c.*) **Slime from the Filter Presses.**—In order to control the operations of the sugar manufacture it is necessary that the slime from the filter presses should be examined periodically. Several cakes produced on different days are taken and brayed in a porcelain mortar. About 150 grams are placed in a flask, with about 500 c.c. of boiling water, and carbonic acid passed into the liquor, kept hot, until all the lime is converted into carbonate. This treatment with carbonic acid has for its object the decomposition of the insoluble sugar lime. The liquor is filtered into a capacious flask, and the precipitate well washed with hot water. The flask is then connected with the exhaust pipe of an air pump and the atmospheric pressure being reduced the liquid can be rapidly evaporated in a water bath without causing the decomposition of the sugar. When the volume is reduced to about 50 c.c., the liquor is poured into a bottle of 100 c.c. capacity, the flask washed with a small quantity of water several times, and the solution cleared with lead acetate. It is then made up to 100 c.c., filtered, and examined in the polarisation apparatus.

(*d.*) **Pressings, and Maceration and Diffusion Residues.**—Care being taken to obtain an average sample, the substance is divided as finely as possible, the pressings by tearing apart, and the diffusion residues by cutting. A quantity of not less than 100 grams is taken, treated with cold water, and lime water or milk of lime added until it has a weak alkaline reaction. After two hours, the solution is poured off and replaced by fresh water. After this has also been poured off, the insoluble portion is collected on a piece of linen and well pressed. The united liquors are filtered through paper and evaporated as above; the residue from the evaporation is saturated with carbonic acid at boiling temperature, filtered to separate carbonate of lime; lead acetate is added and the clear liquor polarised.

(*e.*) **Sugar Beets.**—The beets are converted into a paste with an ordinary hand rasper, the paste enclosed in a linen bag and pressed in a hand press. The residue is taken out and again pressed as sharply as possible, as the juice from the different degrees of pressure has not the same composition; a juice richer in sugar flowing from the slight pressure than from the stronger. Usually only the sugar and non-saccharine matters in the juice are estimated. Immediately after pressing, the juice is tested at the normal temperature with a Brix's saccharometer; the saccharometer should sink to 16°·6. If the saccharometer does not indicate higher than 17°, 100 c.c. of the juice are removed with a pipette and mixed with 10 c.c. basic lead acetate solution. With a higher indication the 100 c.c. of juice is diluted with 100 c.c. of water, and 20 c.c. of lead solution added. After well shaking it is filtered through paper and the clear liquor is placed in the polarisation apparatus. It has to be borne in mind that the volume of juice has been increased one-tenth by the acetate of lead solution, and a correction must be made accordingly. Supposing a juice undiluted with water to give a polarisation of 82·5, in order to find the quantity of sugar in the juice unmixed with lead acetate, the observation has to be increased one-tenth. The polarisation corresponding to the amount of sugar would therefore be $82{\cdot}5 + 8{\cdot}25 = 90{\cdot}75°$. As in a correctly adjusted instrument each degree of polarisation shows a sugar contents of 0·1635 gram in each 100 c.c., such a juice would contain $90{\cdot}75 \times 0{\cdot}1635 = 14{\cdot}84$ grams of sugar in 100 c.c. When the juice has been diluted with 100 c.c. of water, and 20 c.c. of lead acetate solution, the calculation must be made in the same way, but doubling either the final result or the degree of polarisation indicated.

In calculating the weight per cent. the method used is as follows. The saccharometer indication in the previous example was 16·6. Reference to the table on p. 873 shows that this corresponds with a specific gravity of 1·068, 100 c.c. of the juice weigh 106·8 grams and contain 14·84 grams of sugar. Consequently it contains $\frac{14{\cdot}84 \times 100}{106{\cdot}8} = 13{\cdot}9$ per cent. by weight of sugar. The difference between the original saccharometer indication and the amount of sugar represents the amount of non-saccharine matters; in this case it is $16{\cdot}6 - 13{\cdot}9 = 2{\cdot}7$ per cent. The sugar quotient of this juice (see p. 820) would be $\frac{13{\cdot}9}{16{\cdot}6} = 0{\cdot}837$.

It has been already stated that this difference only gives the amount of non-saccharine matter approximately, but sufficiently near for practical purposes. For an exact estimation the amount of dry substance must be determined. For this purpose a weighed quantity of juice (say 100 grams) is diluted with an equal weight of water, and filtered to remove suspended matter, the thick juice being difficult to filter About 20 c.c. are weighed off and evaporated to dryness in a water bath, and the residue afterwards dried at 100° until the weight remains constant. The best way is to stand the dish in a larger one filled with sand heated to 100°, and place them both under the bell of an air pump. The percentage weight of dried substance found has to be doubled in consequence of the dilution. The ash is estimated by the method described for molasses, a larger quantity of juice being taken.

The amount of albuminous substances is determined by evaporating a weighed quantity of the juice to dryness, mixing soda lime with the dry residue, igniting in a combustion tube, and collecting the ammonia formed in titrated sulphuric acid. As albuminous substances contain on the average 16 per cent. of nitrogen, the quantity of nitrogen found is multiplied by 6·5, in order to reduce it to albumin. It being very difficult to remove the dried juice from the sides of the vessel, very small thin glass dishes are used for the evaporation; they have a capacity of 25 c.c. and weigh scarcely 0·5 gram, and are pounded up with the dried residue in a mortar, in order to mix the whole with soda lime without any loss.

Revivification of the Charcoal.—The kilns used for the ignition of the animal charcoal, after being submitted to the treatment described on p. 844, are of various construction. A continuously acting calcining kiln is represented by figs. 640 and 641. In the centre of the brickwork (H H) is a fireplace (E), covered in by an arch, in which

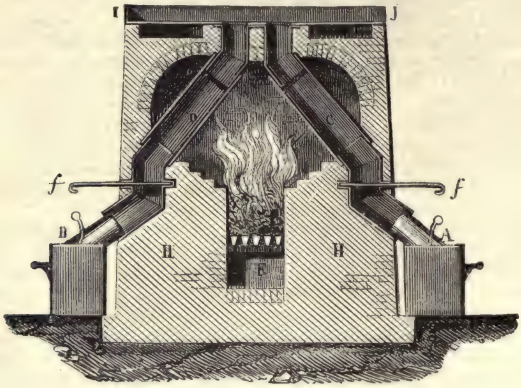


Fig. 640.

are fixed the square chambers (D and C′ D′), the upper ends of which communicate with a shallow tray of sheet iron (I J), extending over the whole area of the kiln. The

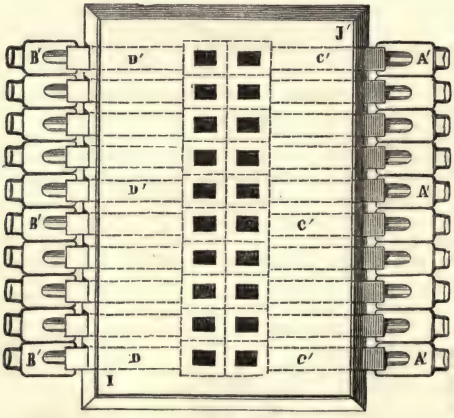


Fig. 641.

flame passes from the furnace through eighteen flues, constructed, in the intervals between the calcining tubes, into an open space under the sheet-iron tray. The lower ends of the calcining tubes are connected with bent tubes, each containing a siding damper (*f*), and with sheet-iron boxes (A A′ B B′) sufficiently large to receive the whole contents of the ignition cylinders. The charcoal is spread out upon the drying surface (I J), and when sufficiently dried is fed into the tubes (C D). The heat is then raised to redness, and when the tubes have been maintained at this temperature for

about half an hour the dampers (*f*) are drawn out, and the calcined charcoal is allowed to fall into the boxes (A A′ and B B′). The dampers are then closed, the tubes again filled, and the operation is repeated every half hour.

A calcining furnace, introduced by Cail, is represented by figs. 642 to 645. On each side of the fireplace (G) are series of flues, through which the hot gas passes from

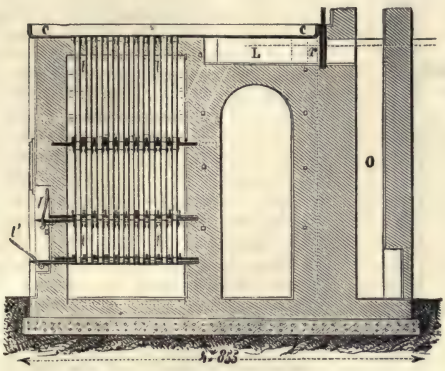


FIG. 642.

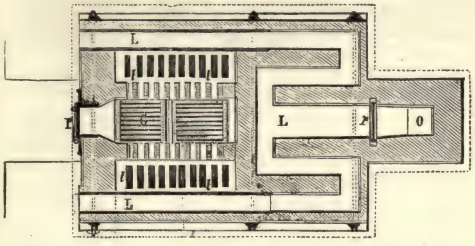


FIG. 643.

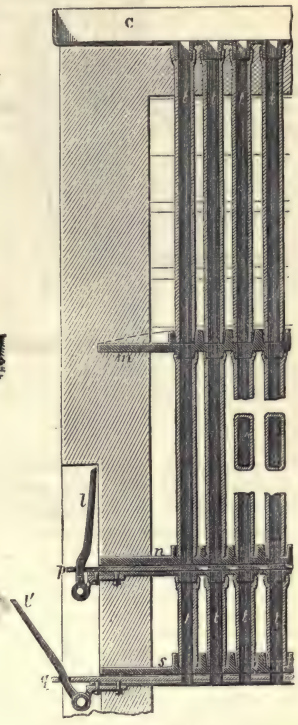


FIG. 644.

the fire to the calcining tubes (*l l*), and then escapes through the flues (L L), under the drying surface (C C), into the chimney (O). Each of the calcining tubes consists of three pieces communicating at one end with the drying floor (C), as shown in the large drawing (fig. 644). The ten tubes on each side of the fireplace can be separated by two dampers (*p q*) into two parts, the lower of which is about one-fifth of the total capacity of the tubes. When the calcining process is commenced the tubes are made red hot, and the sliding damper (*p*) being closed by means of the lever (*l*), the upper parts of the tubes are about half or two-thirds filled with charcoal that has been partially ignited, and then filled up to the top with merely dried charcoal, which is also heaped up above the opening of the tubes upon the drying floor, so that on discharging the charcoal from the lower parts of the tubes the heaps above sink into them. After the lapse of half an hour the sliding damper (*q*) is closed by means of the lever (*l′*), and the damper (*p*) is opened to allow the space between *p* and *q* to become filled with ignited charcoal. The damper (*p*) is again closed, and after the lapse of half an hour the damper (*q*) is opened so as to allow the cooled charcoal to fall into the brick chamber below. The damper (*q*) is then again closed, more

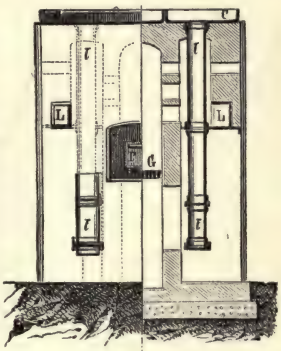


FIG. 645.

ignited charcoal is let down by opening the damper (*p*), this being repeated every half hour. The horizontal section of the calcining tubes is oval, measuring about 10 inches by 3¼ inches, and the distance between the two dampers is about 16 inches.

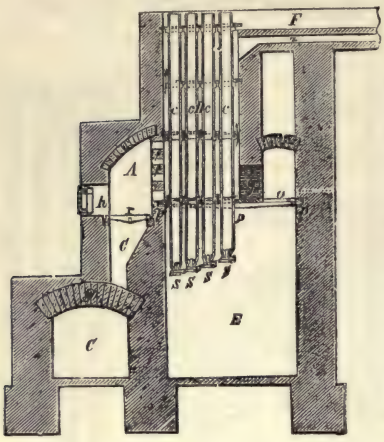


FIG. 646.

Another common form of charcoal kiln is represented in vertical longitudinal section by fig. 646. The fireplace (A), with its grate (*r*) and fire door (*h*), is so placed that the hot gases from the fire pass through the perforated brickwork (*f f*) into the chamber (D) where the calcining cylinders (*c c*) are fixed. These cylinders are most strongly heated at the upper portion of the lower half, and are not at all heated at the lower ends, but are at this part freely exposed to the air so as to become cooled. The hot gas from the fire escapes under the drying floor (F) through the flue (*z*) into the chimney. The charcoal is fed into the cylinders at their upper ends, where it is gradually heated until it reaches that portion of the cylinders where it is fully ignited. About every twenty minutes the dampers (*s s*) by which the lower ends of the tubes are closed are opened so as to allow about one-fourth of the contents of the cylinders to fall into sheet-iron boxes placed beneath, while a further equivalent quantity is fed into the cylinders at their upper ends. In this way the charcoal is gradually heated up to a sufficiently high temperature and then cooled in the lower ends of the cylinders before being discharged.

ALCOHOL.

The term alcohol was formerly restricted to a substance which is the characteristic constituent of wine, beer, and similar fermented beverages; it is now, however, employed not only in this special sense but also as a generic designation of a number of substances analogous to that existing in wine, etc. These substances have all a similar constitution, and may be regarded as the hydrates of organic radicles resembling metals in their chemical relations, or as derivations of hydrocarbons by the replacement of one or more hydrogen atoms by hydroxyl. Thus, for instance, the alcohol of wine may be represented by the formulæ:—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O \qquad \text{or} \qquad C_2H_5\,(OH).$$

Wine alcohol is ordinarily the product of an alteration of sugar under the influence of organised bodies of a low order, called yeast, the change being one instance of that class of phenomena known under the name of fermentation, and the formation of alcohol from sugar takes place according to the following equation:—

$$C_6H_{12}O_6 = 2CO_2 + 2C_2H_6O.$$

Fermentation is a chemical change which takes place in certain organic substances when they are in contact with other nitrogenous organic or organised bodies, called ferments, and by some it is considered that this change is effected without these latter taking any material part in the process. Hence fermentation has been considered to belong to those processes which depend upon so-called contact action.

As to the way in which the yeast ferment acts upon sugar a number of hypotheses have been set up. This much is certain, that the yeast ferment and the sugar must come into contact in order to secure fermentation. On the other hand, it is uncertain whether the products of fermentation are so far due to the vital action of the ferment cells that the sugar is taken up as food into their organism, and there decomposed into alcohol and carbonic acid, etc., or whether the ferment cells contain a substance capable of decomposing sugar, with which the sugar solution comes into contact, possibly by diffusion through the cell membranes. This last hypothesis seems, according to the most recent researches on the subject, to be the true one.

The decomposition in question may be an analytical process, as is the case in alcoholic fermentation (where sugar breaks up into alcohol and carbonic acid) or in the lactic acid fermentation (where sugar breaks up into two molecules of lactic acid). The process may also be synthetical, as in the formation of sugar from starch by means of diastase; finally analysis and synthesis may go on simultaneously, as in the acetic fermentation in which hydrogen is liberated and oxygen absorbed.

As regards the nature of the substances exciting fermentation two kinds may be distinguished.

1. Where the ferment is a nitrogenous organic (non-organised) substance, as for instance protein substances in a state of decomposition, saliva, etc.

2. Where the ferment is an organised body, some low vegetable organism or infusorium, as in the alcoholic, the lactic, and butyric fermentation, etc.

It is probable the way in which the two kinds of ferments act is identical, and that the ferments of the second class, by virtue of their vitality, produce a substance of the nature of the first class, which then itself causes the phenomenon of fermentation either with or without the ferment itself.

In each class of ferments may be further distinguished a number of individual ferments, which differ from one another in their individual nature as well as in their manner of action. Thus diastase converts starch into sugar, decaying cheese converts milk sugar into lactic acid, the protein substances convert sugar into mannite, yeast converts sugar into alcohol and carbonic acid, and mother of vinegar converts alcohol into acetic acid.

Yeast belongs to the organised ferments; it is a kind of fungus consisting of a number of cells linked together like a chain, and differing in form and size. The

individual cells are round or oval, their diameter varies between 0·025 and 0·01 millimetres.

The composition of yeast is shown by the following analyses :—

	Schlossberger		Wagner	
Carbon	50·1	47·9	45·5	52·5
Hydrogen	6·5	6·2	6·2	7·2
Nitrogen	11·18	9·8	9·4	9·7
Oxygen and sulphur . . .	31·6	35·9	38·9	30·6

The ferment cells break up into the characteristic cell substance and the cell contents. The cell substance has the composition of ordinary cellulose; the cell contents consist of a portion which can be dissolved out by means of acetic acid or dilute solution of potash, leaving the cell substance as a residue. Upon the neutralisation of the solvent, the dissolved substance is precipitated, with the loss however of its sulphur. Its composition appears from the following analyses by—

	From Acetic Acid Mulder	From Potash Solution Schlossberger
Carbon	53·3	55·0
Hydrogen	7·0	7·5
Nitrogen	16·0	13·9
Oxygen	23·7	23·6

The ash of yeast consists essentially of phosphoric acid and potash, with small quantities of magnesia and lime. It amounts to about 7½ per cent. of the weight of the yeast.

Formation of Yeast.—The formation of yeast is assumed to depend upon the presence of germs and spores suspended in the air, which begin to develop when they fall into liquids suitable in containing the nutriment necessary to their propagation.

The presence in the air of germs necessary for bringing about the propagation of yeast has been inferred by the following experiment by M. Pasteur:—

A solution of sugar containing the necessary food for yeast germs is boiled in a glass flask long enough to secure the destruction of all germs and spores previously contained in the liquid, as well as to drive out the air in the neck of the flask and replace it by steam, whereupon the neck of the flask is sealed. A flask thus prepared may be left for weeks at the temperature (30° to 33°) most suitable for the propagation of yeast without any formation of ferment or fermentation; on the other hand, both formation of ferment and fermentation begin directly the flask is opened and exposed to the air, especially when a little dust is thrown into the flask.

The food of the yeast plant consists of carbonaceous and nitrogenous substances, as well as of those inorganic substances found in the ash of yeast, which are chiefly potash and phosphoric acid. Sugar serves as the carbonaceous constituent; the nitrogenous and inorganic substances are contained in the juice of most plants or extracts prepared from them, the first in the form of albuminoids, the latter in the form of various salts.

A liquid capable of supporting yeast vegetation may be artificially prepared by dissolving sugar and ammonium tartrate in water, adding a small quantity of potassium carbonate and glacial phosphoric acid, then saturating the liquid with carbonic acid, and finally adding a very small quantity of calcium carbonate and of magnesium carbonate.

The growth of yeast is stopped by the addition of strong mineral acids or large quantities of organic acids, also by salt, sulphur, and a number of other reagents; small quantities of organic acids are however not prejudicial.

All kinds of sugar are not capable of undergoing alcoholic fermentation. The kinds of sugar usually employed in carrying on fermentation industrially, namely grape and fruit sugar, are capable of direct fermentation. On the other hand, cane sugar and milk sugar have not the power of direct fermentation, but may easily be converted into fermentable sugar. This transformation may be effected either by treatment with acids or by prolonged contact with large quantities of yeast. The conversion of cane sugar into fermentable sugar is designated inversion, and is a change analogous to fermentation.

The process of fermentation is unequally rapid in proportion to the quantity of

sugar in solution, the most favourable proportion of sugar in a solution being 12 per cent.; more sugar hinders the fermentation.

Not only an excess of sugar but an excess of alcohol also retards the progress of fermentation, so that in a solution containing much sugar, after a certain quantity of alcohol is formed by fermentation, the remaining sugar ceases to ferment, because the further fermentation is hindered by the alcohol.

The relative proportions of sugar and yeast also influence the duration of the fermentation. In practice, in order to secure quick fermentation, the proportions used are 5 parts of sugar to 1 of yeast, although the same quantity of yeast is capable of fermenting a much greater quantity of sugar.

The phenomena of fermentation also differ with the temperatures at which it is allowed to take place. Up to a certain point the rapidity of the fermentation increases with the temperature, but when a temperature of 33° is reached, the fermentation becomes slower, and a further rise stops it altogether.

When fermentation is conducted at a low temperature the yeast employed remains at the bottom of the fermenting liquor, and this fermentation is known as sedimentary fermentation. This kind is considerably employed industrially; the most suitable temperature for conducting it being between 5° and 10°.

The other kind of fermentation, which is conducted at a temperature of between 10° and 24°, is more rapid, and is known as surface fermentation, owing to the fact that the yeast cells rise to the surface in consequence of the strong development of carbonic acid.

The products of the fermentation of sugar with yeast—alcoholic fermentation—are chiefly alcohol and carbonic acid.

About 5–6 per cent. of the sugar is, however, decomposed into glycerin, succinic acid, and carbonic acid, yielding at the same time material for the formation of the yeast cells. The quantities in which the latter substances are produced are, according to Pasteur, as follow:—

Succinic acid	0·6–0·7 per cent.
Glycerin	3·2–3·6 „ „
Carbonic acid	0·6–0·7 „ „
Cellulose and fatty substances	1·2–1·5 „ „

Pressed Yeast.—For purposes of storing, yeast is deprived of the greater part of its water and other impurities, by a process of washing and pressing, the product being known as pressed yeast. Surface yeast is most suited for this purpose.

The yeast is pressed through linen or a hair sieve, so as to remove particles of hops and other impurities; the filtered liquid is then allowed to stand whilst the yeast settles to the bottom. The supernatant liquid is then decanted off; the yeast treated with a fresh quantity of cold water, and the whole thoroughly stirred up. These operations of decanting and washing are repeated until the wash water ceases to give an acid reaction. The thoroughly washed yeast is finally mixed with 15 to 30 per cent. its weight of starch, filled into sacks and pressed. This pressed yeast comes into the market in lumps of a pound in weight, whence it is sometimes called pound yeast.

Artificial Yeast.—The consumption of yeast is so great that frequently it is manufactured by itself. For this purpose thin mash, or still better, clear wort, is employed to which, in order to secure the formation of yeast cells, as much as possible of the nitrogenous compound of malt is added; a small quantity of sulphuric acid—about ½–1 per cent. of the weight of groats is employed—previously diluted with water, being added to the solution of gluten. Artificial yeast is much used in distilleries; a more detailed account of its preparation will therefore be given under that head.

In what has preceded, the results attending the vinous fermentation have been detailed, but fermentation is a process in nowise limited to carbohydrates of the class of grape sugar, neither is it dependent upon one particular ferment. For instance, ordinary yeast does not consist only of the cells of *Torula cerevisiæ*, but also contains some of *Penicillium glaucum*; these last may be separated in some measure by shaking up yeast with water and filtering; the *Torula* cells, being the larger, are retained by the filter, and when added to a sugar solution, they cause the alcoholic fermentation, but the filtrate containing the cells of *Penicillium*, if added to a sugar solution, causes the lactic fermentation to set in.

Again, an aqueous extract of yeast rapidly converts cane sugar into dextrose and lævulose, but cannot further influence it.

This last process is suggestive of that form of fermentation which is supposed by Bernard and others to cause the transformation of liver glycogen or dextrine into glucose—in itself merely a process of hydration. But Pasteur and his disciples consider this act due to the influence of a special ferment in the blood, which, while it causes this change, reproduces itself from a part of the material influenced by it.

Not so, however, did Liebig regard such processes of fermentation; it was sufficient for him that the conditions necessary for starch to take up a molecule of water were present; he did not perceive the necessity of believing the result due to a form of life, all that was required being the presence, and the contact of a substance itself in process of change. Thus he compared such processes to the decomposition of argentic oxide caused by its contact with peroxide of hydrogen. The latter body being unstable and slowly undergoing decomposition, influences the oxide of silver in a similar manner, and the contact action is therefore expressed by the equation $H_2O_2 + Ag_2O = H_2O + Ag_2 + O_2$.

Here it is that Pasteur and Liebig differed. Pasteur regards all processes of fermentation as essentially 'correlative phenomena of a vital act; beginning and ending with it;' so that wherever there is fermentation, there is also organisation, development, and multiplication of the globules of the living ferment. Liebig never admitted the necessity of the living element. But after all, the difference between these two views is but slight; in both the direct cause is *something in change*; whether that change be essentially connected with the function of life possessed by cells and spores is a matter not even yet decided.

It is not possible nor desirable here to enter into a further consideration of the life processes of yeast. It is sufficient to remember that in a large measure the conditions upon which the life, health, and disease of cells depend have been established, and it has even been demonstrated by Pasteur that yeast, like higher forms of life, breathes.

There are many other media in which yeast excites a process of decomposition, but, so far as observed, malic acid is the only plant acid which admits of the multiplication of the yeast cell. When a mixture of calcic malate with water and yeast is set aside in a warm place, the acid is split up into succinic, acetic, and carbonic acid and water, thus:

$$3C_4H_6O_5 = 2C_4H_6O_4 + C_2H_4O_2 + 2CO_2 + H_2O.$$

If the temperature rises beyond a certain point, hydrogen is evolved and butyric acid is formed. Again, if a solution of cane sugar or milk sugar be mixed with stale cheese or milk, and chalk, and kept at 30°–35°, the sugar is gradually converted into lactic acid, and the process is termed the lactic fermentation, $C_6H_{12}O_6 = 2C_3H_6O_3$; the chalk merely serves to neutralise the acid as it forms, otherwise its presence would stop the fermentation. When this change is completed, the calcic lactate gradually disappears, and butyrate is formed, while hydrogen is evolved; other products also accompany the butyrate of lime.

Another form of fermentation and one well known is the acetous, which consists in the transformation of alcohol into acetic acid, by the agency of the ferment *Mycoderma aceti*. This change is one of oxidation only, and it appears that the ferment acts like spongy platinum, viz. as a carrier of oxygen.

There are many other processes of fermentation, among which that termed mucous fermentation is induced in sugar by some nitrogenous substances, and terminates in the production of mannite, lactic acid, and hydrogen, together with carbonic anhydride.

Emulsin (a nitrogenous constituent of bitter almonds) also splits up amygdalin into benzoic aldehyde, glucose, and hydrocyanic acid. The ptyaline of saliva converts starch into glucose; the pepsine of the gastric juice renders soluble the albuminous constituents of food, with some slight change. All these may be regarded as fermentative changes, just in the same way also as putrefaction is of the same nature. When albuminous substances are allowed to putrefy by contact with the air, in the presence of moisture, the albumin is decomposed, yielding a number of products which are identical with those obtained from the same substance, by a combined chemical process of oxidation and hydration. That is to say, the changes induced by fermentation are of an ordinary chemical type, and it is only by chemical means that it can be decided whether such changes are primarily due to the presence of living organisms, or whether that is merely a coincident circumstance.

In the case of albumin, for instance, a knowledge of its composition and of its decomposition products, as well as the total products induced by what is termed fermentation or putrefaction, may make it possible to decide upon the measure of the influence exerted by cell life in the process. Albumin is a complex substance liable to change; exposed to the air and moisture it is speedily contaminated with germs and spores; in their nutrition the albumin is finally quite destroyed by oxidation and hydration.

A word may here be said appropriately concerning antiseptics. Albumin in a combined state is not nearly so prone to change as when in a free state, so that if it be possible to effect such combination, or if it be possible to shroud the albumin from oxygen in any way; as, for instance, by enveloping it with a medium of an agent not

penetrable by oxygen, or having a greater affinity for oxygen than albumin has, then the albumin may be preserved from change, and in so far the agent employed for this purpose becomes an antiseptic.

Characters.—Alcohol is a colourless liquid, having a peculiar agreeable odour and a burning taste. In the raw state, as it is obtained by distillation of fermented liquors, the smell and taste are modified by the presence of other substances, which are formed at the same time with alcohol in the process of fermentation, and are collectively designated fusel oil. In a diluted state, alcohol has an agreeable taste. Mixtures of about equal parts of alcohol and water, with various flavouring substances in small proportion, constitute the different kinds of spirits used for drinking. In this state, alcohol exerts a peculiar stimulating influence upon the nervous system, and in large doses it produces intoxication and stupor. The action of all alcoholic beverages is due to the alcohol they contain. In a concentrated state, alcohol acts as a poison.

The specific gravity of alcohol at a temperature of 15° is 0·7947, and at 0° it is 0·8064; its specific heat is 0·615, as compared with that of water taken as unity, according to Kopp; and the latent heat of vaporisation is 208·92, while that of water is 536·5. Alcohol boils at 78·°4 under a barometric pressure equal to 0·760. This low boiling point of alcohol admits of the separation of alcohol from water by distillation, and by reason of the low specific heat, as well as the low latent heat, it is possible to increase the strength of a mixture of alcohol vapour and water by abstracting part of its heat, the effect being the condensation of water vapour chiefly, while the alcohol remains uncondensed. Alcohol vaporises to some extent, at all temperatures, and on this account there is liability to loss when alcoholic liquids are kept.

The vapour of alcohol is inflammable even when mixed with air, and therefore care must be taken to avoid bringing a light near to it; neglect of this precaution has often given rise to serious accidents. Alcohol is also readily inflammable in the liquid state, and it burns with a bluish flame, emitting but little light. The presence of foreign substances communicates to the flame of alcohol characteristic colours; sodium salts produce a yellow colour, strontium salts a purple red colour, calcium salts a yellowish red, and copper salts a green colour.

Alcohol is miscible with water in all proportions, and in the pure state it has such an attraction for water, that it absorbs it from the atmosphere. On mixing alcohol with water heat is evolved, and after cooling there is a considerable contraction of volume, so that the bulk of the mixture is always less than the joint bulk of the separate liquids. This contraction is greatest when 53·7 parts by measure of alcohol are mixed with 49·8 parts of water, and the volume of the mixture is 100 parts instead of 103·5. By reason of this contraction, the specific gravity of mixtures of alcohol and water does not correspond with the proportions of the two liquids. The relations between the specific gravities of such mixtures, and the relative amounts of water and alcohol, have been studied by Gilpin and Gay-Lussac, and tables have been constructed by which these data can be ascertained, those of Tralles referring to a temperature of $15°\frac{5}{9}$ (60° F.), while those of Gay-Lussac refer to a temperature of 15°. In order to obviate the use of specific gravity determinations and tables indicating the corresponding amounts of alcohol and water, aerometers have been constructed, by means of which the amount of alcohol may be directly ascertained. In France, Gay-Lussac's alcoholometer is employed, and in Germany that of Tralles. Both indicate differences of specific gravity which are in excess of those that may result from temperature within the ordinary range of variation, but Tralles' alcoholometer is most to be depended upon for accuracy. Besides the alcoholometer of Gay-Lussac, there is another instrument used in France, that of Carlier, which is constructed upon a purely empirical basis. The scale is divided into 44 parts or degrees, and immersion to 10° represents the specific gravity of water, while 44° represents the specific gravity of absolute alcohol. A further difference between this instrument and others consists in the observation of gravities being conducted at a temperature of 12°·5.

Sykes's hydrometer is the one officially employed in this country; it is made of metal, and has a four-sided stem divided into eleven equal parts, which fits into a hollow brass ball, while at the opposite side of the ball there is another stem of sufficient weight to make the instrument float upright in a liquid, and shaped in such a manner that the weights for loading the stem can be slipped upon it. The instrument is adjusted to float with the zero of the scale, in spirit of specific gravity 0·825 at 60° F. (15·6), coinciding with the surface of the liquid. The mixture of alcohol and water having this density contains 89 per cent. by weight of absolute alcohol, and it is the standard alcohol of the Excise. In weaker spirit the instrument does not sink so low, and if the density of the liquid be much greater, it is necessary to hang one of the weights upon the lower stem, in order to cause the immersion of the bulb.

In France the strength or alcoholic contents of liquids is expressed as follows:

	Cartier	Gay-Lussac
Anhydrous or absolute alcohol	44	100
Rectified spirit	39	94·1
" "	36	89·6
Wine spirit	33	84·4
" "	22	58·7
" "	21·6	58·
Brandy (Cognac)	20	52·5
Ordinary spirit	19	49·1
Weak "	18	45·5

In Germany the value of alcoholic liquids is indicated by the amount of pure alcohol; spirit of 80 per cent. for instance is a mixture of alcohol and water, containing 80 per cent. by volume of anhydrous alcohol measured at a temperature of $15°\frac{5}{9}$ ($=12°\frac{4}{9}$ R. or 60° F.)

Strong alcohol is a powerful solvent of many substances; it dissolves the hydrates and the sulphides of the alkali metals, and many salts, especially those which are deliquescent, such as calcium chloride, magnesium chloride, strontium chloride, calcium nitrate, and magnesium nitrate, but strontium nitrate is insoluble in alcohol.

Mercuric chloride is dissolved by alcohol more readily than by water; mercuric bromide and mercuric iodide are likewise soluble in alcohol. Many other salts which are soluble in water do not dissolve in alcohol; and this character is often taken advantage of in analysis for effecting the separation of substances, as well as in the purification of some preparations. Substances that are soluble in water but insoluble in alcohol may sometimes be precipitated from their aqueous solutions by the addition of alcohol. The solubility of calcium nitrate in alcohol is applied technically for separating this salt from strontium nitrate. Ferrous sulphate is insoluble in alcohol, and in order to prepare this salt in a pure state it is precipitated from the aqueous solution by adding alcohol. Many organic substances which are insoluble in water dissolve readily in alcohol, as, for instance, ethereal oils, most resins, and vegetable alkaloids, the fat acids, some fat oils, hydrocarbons, paraffin, camphor, soap, etc.

The alcoholic solutions of ethereal oils are used in preparing the solutions of resins, in varnishes; the solubility of vegetable alkaloids is taken advantage of in the preparation of these substances, and by the evaporation of an alcoholic solution of soap the material known as transparent soap is obtained.

Concentrated alcoholic solutions of some salts deposit, on cooling, crystals which contain alcohol as a constituent, in the same manner that water is sometimes a constituent of crystallised salt. Compounds of this kind were termed by Graham **alcoholates**.

The chemical action of substances upon each other is sometimes modified by alcohol, according to the solubility or insolubility of the substances to which they are capable of giving rise. Thus when carbon dioxide is passed into an alcoholic solution of potassium acetate, potassium bicarbonate is precipitated, and acetic acid is produced. In aqueous solutions, however, all carbonates are readily decomposed by acetic acid.

Under the influence of atmospheric oxygen, alcohol undergoes a gradual decomposition, and is converted into acetic acid; but this change takes place only to a slight extent when the alcohol is not very much diluted with water. Very dilute alcoholic liquids when distributed throughout porous substances, so as to expose an extended surface of contact with the atmosphere, rapidly absorb oxygen, and the alcohol they contain is thus converted into acetic acid. The preparation of vinegar by what is termed the quick process depends upon this fact.

By the mutual reaction of concentrated sulphuric acid and alcohol at the ordinary temperature, there is formed **ethyl-sulphuric acid**, and when this substance is heated with an excess of sulphuric acid to a temperature of 140°, while a stream of alcohol is allowed to flow slowly into the mixture, decomposition takes place, **ether** and water being formed which distill over together; and by suitably regulating the supply of alcohol, as well as the temperature of the mixture, the sulphuric acid is but very slightly altered. When the temperature is raised above the point mentioned, a further decomposition takes place, and the alcohol is converted into **olefiant gas**.

Preparation.—In order to obtain pure absolute alcohol, the spirit resulting from the distillation of any fermented liquors must be first subjected to various operations for the purpose of purifying and concentrating it. The product thus obtained constitutes the **rectified spirit** of commerce, which should be free from other alcohol, and contain no more than from five to eight per cent. of water. This amount of water cannot be separated from alcohol by mere distillation, and the complete dehydration can only be effected by bringing the alcohol into contact with substances

which combine chemically with water, and form compounds that are not again decomposed at the temperature of boiling alcohol. Thus, for instance, when alcohol containing water is mixed with quicklime, the water is abstracted by reason of the formation of calcium hydrate, from which the alcohol may then be separated by distillation. Another plan of abstracting the water from dilute alcohol consists in mixing it with cupric sulphate, from which the water of crystallisation has been separated by heating the salt. After some time, the water in the alcohol is taken up by the cupric sulphate. Calcium chloride in a dry state acts in the same manner. Alcohol may be to a great extent deprived of water by these substances; but when quicklime is used for the purpose, the product often has a disagreeable smell and taste, which may be due to the action of the lime upon some foreign substance in the spirit, or to a slight decomposition of the alcohol itself.

In preparing absolute alcohol on a small scale, cupric sulphate may be conveniently used. For this purpose, the coarsely powdered salt is heated in an iron pan until its blue colour disappears, and it is converted into an almost white powder, consisting of anhydrous cupric sulphate. A quantity of this powder is placed in a flask and covered with rectified spirit, the flask closed with a cork, and the mixture left to digest for about twenty-four hours with occasional agitation. According to the amount of water in the rectified spirit, the cupric sulphate combines with it more or less rapidly, and again acquires the blue colour of the hydrated salt. When this has taken place, the flask is connected with a condenser heated in a water bath, and the alcohol distilled off.

Raw Materials.—Any material may be used for obtaining alcohol which contains alcohol ready formed, or fermentable sugar, or even sugar and other substances that are not susceptible of fermentation, provided they are capable of being converted into fermentable sugar. Thus wine, beer, cider, etc., may be used on account of the spirit they contain; the various kinds of fruit may be used on account of the grape sugar and fruit sugar they contain; beet root and molasses as containing cane sugar; milk also as containing lactose; potatoes, the grain of cereals, and many other kinds of seed, on account of the starch they contain; and even wood may be used for this purpose, inasmuch as the cellulose it contains can be converted into grape sugar.

Various considerations, however, have to be taken into account in selecting a material for the production of alcohol. In general, that material would be preferable which under given conditions would furnish the largest amount of alcohol with the least expense. But, on the other hand, certain objects for which the spirit is to be used must be considered. If a drinkable product is to be produced, only such raw materials can be used as are capable of satisfying this requirement; hence, wine is used to prepare brandy, and cherries to prepare a similar spirit known as Kirschwasser, the higher value of the product making up for the cost of the raw material. Besides these circumstances, there may also be others of a more artificial nature which preclude the possibility of using certain materials. Thus the duty levied upon spirit in many countries renders it impracticable to use other materials for producing alcoholic products than those which yield a considerable amount of alcohol in proportion to their bulk.

The method of procedure followed in the manufacture of spirit varies according to the nature of the raw material operated upon.

Treatment of Alcoholic Liquors.—In this case all that is necessary is to separate the alcohol already existing in the liquids from the other substances mixed with it, partly volatile and partly fixed, and then to obtain the alcohol in a concentrated condition. This is effected by distillation. Alcohol, as already mentioned, has a lower boiling point and a lower latent heat of vaporisation than water has. When, therefore, a liquid containing but a small amount of alcohol is heated and kept for some time at the boiling point, a mixture of alcohol vapour and water vapour is formed, which is under all conditions proportionately richer in alcohol than the original liquid, and after some time the liquid remaining is free from alcohol. If the vapour be condensed, a liquid is thus obtained which is free from non-volatile substances, and contains alcohol and water in varying proportions, according to the time the distillation has been carried on. It may be assumed in general that, in order to obtain all the alcohol from fermented liquors by distillation, about one-third of the volume of the liquid must be vaporised. The residue thus freed from alcohol is termed spent wash. The distillate obtained is termed low wine, and unless the distillation has been stopped at an early stage, as is sometimes requisite, it contains alcohol and water in such proportions that the amount of alcohol is not sufficient to admit of the product being used at once as a beverage; it contains moreover substances which, though possessing in a pure state a boiling point much higher than that of alcohol, have the property of distilling over to some extent together with water vapour. These

substances are comprised under the general term fusel oil. The one among them that is best known is amyl alcohol, which is produced especially in the fermentation of amylaceous substances. The constituents of fusel oil have generally an extremely disagreeable smell and taste, and their presence deteriorates the quality of spirituous liquors. Some of these substances, on the contrary, are distinguished by their great aroma, and therefore their preservation is requisite for giving a high quality to the spirit. When this is the case, the distillation is conducted in such a manner that the collection of the distillate is stopped as soon as it begins to be diluted by the condensation of water vapour to a greater degree than corresponds to the strength of the spirituous liquor required. Loss of alcohol would thus be entailed, unless the alcohol still remaining in the liquid undergoing distillation were distilled off; this is therefore collected in a separate receiver under the name of after wine, and is added to the liquid to be distilled in the subsequent operation.

In most cases, it is necessary to submit the product of the first distillation to further concentration and purification. Besides the fusel oil above mentioned, it contains some substances the boiling points of which are lower than that of alcohol; such as aldehyd, various ethers, etc., formed by the alteration of alcohol. These substances communicate to the spirit a fiery taste, and consequently they must be removed. The purification of the low wine is effected by distillation, which is termed rectification. In this operation heat is at first applied gradually, in order to remove the most volatile of the foreign substances from the spirit, and to concentrate them in the first portion of the distillate. As soon as the spirit distilling over is free from objectionable odour, the receiver is changed, and the spirit is then collected as long as it is of sufficient strength. The receiver is then changed again, and the remainder of the alcohol collected apart as weak spirit, which always contains much fusel oil. The first and last runnings are mixed together and again distilled with a fresh charge.

When strong spirit is required, the rectification is sometimes repeated several times, and the first and last portion of each distillate are collected apart. This method of operation involves considerable expenditure of fuel and labour, as well as much loss of alcohol; and as methods are now known by which these disadvantages may be avoided, the direct production of spirit is practised only when it is desirable to preserve the peculiar aroma of the fermented liquors, as in the manufacture of brandy, or when the operation is carried out on such a small scale that the erection of costly plant is not practicable. In far the great number of cases, it is customary with the improved forms of apparatus to produce, at the outset, spirit containing but little fusel oil, and of a strength equal to at least 80 per cent. alcohol: this is further purified and concentrated by rectification, and then reduced by admixture of water to the strength required for use.

The principle upon which the apparatus used for this purpose is constructed is the following. In a mixture of alcohol vapour and water vapour, there are two substances which differ considerably in regard to the amount of heat they require for maintaining the condition of vapour. The latent heat of water is much higher than that of alcohol. When such a mixture is cooled and part of the heat abstracted from it, part of the vapour is condensed to the liquid state. But since alcohol requires much less heat in order to maintain the form of vapour than water does, it is evident that, by the abstraction of heat, that portion of the mixed vapour must be first condensed which requires the greatest amount of heat for its maintenance; in other words, the water is first condensed, and in consequence of this the mixed vapour is rendered poorer in water and richer in alcohol. If this process is repeated often enough, the condensation of the water and the concentration of the alcohol continue until a point is reached at which the mixture consists chiefly of alcohol vapour, and only contains a small proportion of water vapour, and the condensation of the whole remaining vapour then furnishes strong spirit.

A large variety of variously constructed distillatory apparatus are based upon this behaviour of the mixed vapour, and though they present very different external deviations of arrangement, their operation is essentially referable to the same principle. In all cases, the liquid to be distilled in such forms of apparatus is heated either by direct fire, or by high-pressure steam, or by injection of steam. The mixture of water vapour with a small proportion of alcohol vapour thus produced is passed into a second vessel with the liquid to be distilled, either cold, or already heated to a certain degree. According to the temperature of the vapour and that of the liquid, in the second vessel a certain portion of the vapour is condensed, but that part of the vapour which requires the greatest amount of heat is always condensed in the largest proportion. The mixed vapours subsequently passed into the second vessel have then sufficient heat to convert into vapour not only the alcohol, at first condensed together with water, but also the alcohol originally contained in the liquid, in

the second vessel. The vapour thus produced, and containing a large amount of alcohol, is passed in a similar manner into a third, fourth, and fifth vessel, each of which is charged with the liquid to be distilled, and the result is that there is a progressive condensation of water vapour, and a simultaneous increase in the proportion of alcohol vapour. The operation may also be conducted in such a way that the vaporisation of fresh quantities of alcohol is not attempted, but the mixed vapour is rendered richer in alcohol by abstracting water from it by condensation, until at last it is conducted into an empty vessel surrounded by a liquid, at a temperature between the boiling point of alcohol and that of water. By this means the vapour is so far cooled, that a large proportion of water is condensed with only a small proportion of alcohol, and if this is repeated often enough, the vapour ultimately remaining uncondensed will have almost any desired amount of alcohol.

Apparatus used in Distillation.—The oldest apparatus, which was widely used until within the last thirty or forty years, consisted of a retort-shaped vessel, heated by an open fire, and connected with a coil of pipes lying in a wooden vat, surrounded by cold water. Such an apparatus could only be worked in the production of low wine, the distillation of the low wine to weak spirit, and the rectification of the spirit. The first improvements were made by the French manufacturers, who were soon followed by the Germans. Each had to keep in view the material of their respective countries, in the one case wine, and in the other a material far more difficult to work, the thick mash from grain and potatoes with their skins and refuse.

The first improvement appears to have been originated by Argand. He placed a coil of pipe immediately over the retort or still in a vessel filled with wine, so that the vapour passing from the still into the lower part of this pipe was there partially condensed, and the condensed portion, consisting principally of water, flowed back into the still, whilst the more alcoholic vapour passed upwards, heating the wine in the cooling vessel, and then, entering another worm surrounded by cold water, being there perfectly condensed. In this way strong spirit was obtained in one operation. The heated wine was then run into the retort and used for the next distillation.

The same principle was adopted by Dorn, with the difference, however, that the distillate condensed in the first cooling pipe did not flow back into the still, but was collected in a special receiver where it underwent rectification by fresh vapour, so that a

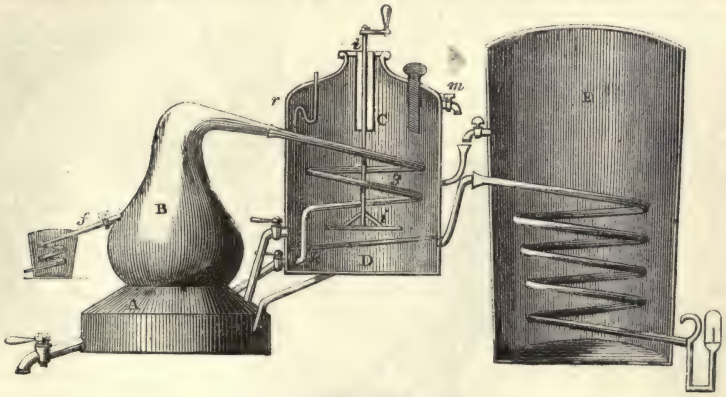


Fig. 647.

liquid nearly free from alcohol had to be worked up with the already heated mash in the next distillation.

This arrangement is represented by fig. 647. The body (A) of the still is surmounted by a capacious head (B), from which the vapour is conveyed by the neck (*r*) to the worm in the vessel (C D), separated by a partition into two compartments, the upper one serving as a heater for the wash, while the lower one acts as a rectifier. The compartment (C) when filled to the level of the tap (*m*) contains the quantity of wash for charging the still. The vapour passing from the still is at first condensed in passing through the worm (*g*), and flows into the compartment (D). When the contents of the compartment (C) have become so hot that no more condensation occurs in the worm (*g*), the vapour bubbles through the liquid in the compartment (D), and heating it to the boiling point drives off alcohol vapour, which is then condensed in the worm of the condenser (E). By means of the pipe (*f*) connected with the small refri-

gerator, the strength of the distillate passing from the still can be tested from time to time.

Edward Adam made the following modification. The still was connected with a series of ovoid metal vessels by a pipe that ended in a rose almost at the bottom of the first vessel. Another pipe connected the upper part of the first vessel with the lower part of the second, and the other vessels were similarly connected. From the last the vapour, which by this time had become very rich in alcohol, passed into the cooling worm. Through the radiation of heat from the surface of the ovoid vessels, causing a corresponding condensation, a part of the mixed vapour was withdrawn, but the succeeding vapour, passing through this liquid, took up and carried forward a part of the alcohol. At the close of the distillation, each condensing vessel contained an alcoholic liquid of higher concentration in proportion as it was further from the still. In order to improve this the contents of the first vessel were emptied into the retort; the second into the first, and so on, so that in the next distillation the previously condensed liquid underwent further rectification.

Cellier-Blumenthal introduced the continuous apparatus, in which the condensation is effected exclusively by the wine to be distilled; the essential novelty being that there is a continual inflow of wine at one end, whilst the spent liquid is discharged from the apparatus underneath in a continual stream. It is a disadvantage of this apparatus that the effluent spent liquor is not quite free from alcohol; but this has been overcome by Derosne's arrangement, in which the outflow is made intermittent whilst the inflow is continual.

Simultaneously, Pistorius introduced into Germany an apparatus consisting of two connected stills, placed one under the other, and provided with a preliminary warmer. Adams's series of condensing vessels was adopted, but instead of being ovoid they were in the form of shallow basins; the condensed liquid too, instead of being collected, flowed back directly into the distilling apparatus. Pistorius's apparatus, with numerous modifications, is now found in almost all German distilleries; but it has lately come into strong competition with one made upon the Cellier-Blumenthal and Derosne principle, and arranged for the working of thick mash.

The heating of distillatory apparatus by steam was introduced in 1829 by Gall.

One of the simplest arrangements admitting of a continuous supply of the liquid to be distilled and an intermittent discharge of the spent wash is that of Laugier,

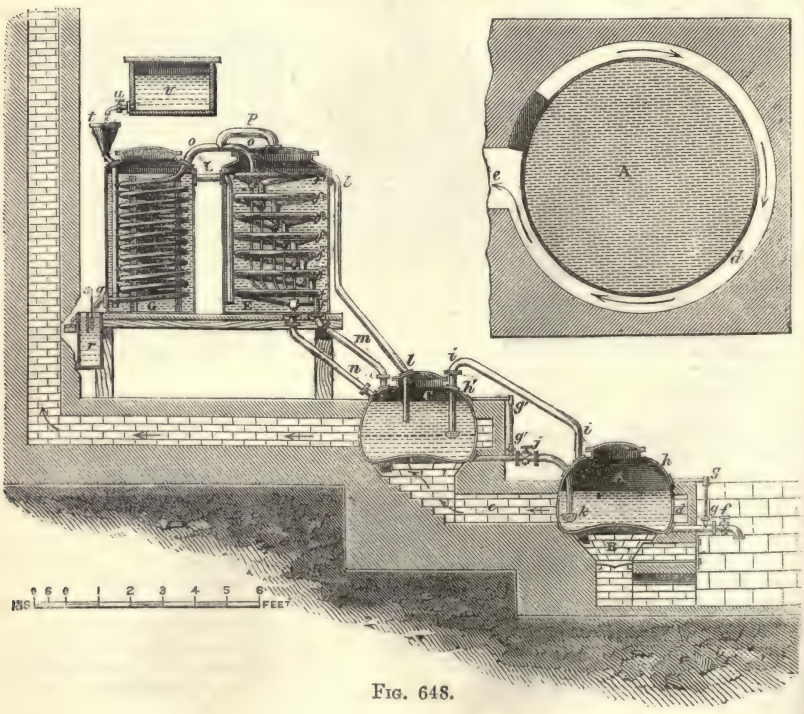


Fig. 648.

represented by fig. 648. It consists of two stills (A C), a dephlegmator (E), and a condenser (G). The still (A) is set over a furnace (B), the flue of which (*c d e*) is continued under and round the second still (E). The two stills are connected together by the tube (*j*) fitted with a valve by which the communication can be opened or shut at pleasure. They are also connected together by the pipe (*i i*), by which the steam generated in the still (A) is passed into the liquid contained in the still (C). The still (C) is connected with the worm of the dephlegmator (E), by the pipe (*m*), and the liquid condensed in each of the coils (*f* to f_7) is run off through a small pipe attached to the lowest part of the coil into a common discharge-pipe (*n*), which is connected with the still (C), so that the condensed liquor is discharged into it. The vapour that is not condensed passes from one coil to the other through the upright connecting pieces until it reaches the tube (*o o*) connected with the worm of the condenser (G), and being there condensed is delivered through the outlet pipe (*q*) into the receiver (*r*) in which an alcoholometer (*s*) floats, and flows away to the store vessels. The liquid to be distilled travels in the opposite direction. It is supplied from the reservoir (*v*) through the tap (*u*) into the funnel tube (*t*) of the condenser (G), and being delivered into this vessel at the bottom displaces its contents through the pipe (L), serving to condense the alcohol vapour passing through the worm of the condenser, and thus becomes heated itself before it escapes through the pipe (L) into the dephlegmator (E), where it is delivered at the bottom, and after filling this vessel escapes in a heated condition through the overflow pipe (*l*) connected with the still (C), into which the heated liquor to be distilled is thus supplied. From this still the liquor can be discharged as required into the still (A) by opening the valve in the pipe (*j*). By means of the tap (*f*) the spent wash can be discharged from the still (A). Both stills are fitted with glass gauges (*g g h*) to indicate the level of the liquid contained in them. The liquor in the dephlegmator (E) is sufficiently hot to give off alcohol vapour, which is conveyed by a pipe (*p*) into the pipe (*o*) connected with the worm of the condenser. The working of this apparatus is very simple. On opening the tap (*u*) of the reservoir the liquid to be distilled flows into the condenser (G), and, when that is full, into the dephlegmator (E), and from thence into the still (C). As soon as the liquor in the still reaches the level of the steam pipe (*i*), indicated by a mark on the gauge glass (*g*), the tap (*u*) of the reservoir is closed, and the still (A) is filled to three-fourths of its capacity with the liquid to be distilled, which is then heated to boiling. The heating is continued until about two-thirds or three-fourths of the liquid is distilled off, according to its alcoholic contents. During this distillation the greater part of the vapour is condensed in the still (C) and in the dephlegmator, but very little alcohol passes over through the worm of the condenser, because the contents of the still (C), as well as the liquid in the dephlegmator, are not sufficiently heated. When the contents of the still (A) are exhausted of alcohol, the tap (*f*) is opened and the spent wash run off; the valve (*j*) is then opened, and the contents of the still (C) run into the still (A). After closing the valve (*j*), the fire is increased so as to bring the hot liquid rapidly to boiling. The tap (*u*) of the reservoir is then opened, and the liquor to be distilled is allowed to run in a slow continuous stream into the apparatus, displacing the slightly warmed liquid in the condenser into the dephlegmator, and driving the still more heated contents of the latter into the still (C), which also receives the hot liquid from the tubes (f_1 to f_7). The supply of liquid to be distilled is so regulated that the still (C) is filled by the time the liquid in the still (A) has been completely deprived of alcohol. This requires about three-quarters of an hour to an hour. The spent wash is then run off, and the contents of the still (C) transferred to the still (A) as before. In this way the operation once started goes on continuously. The liquor to be distilled, flowing continuously into the still (C), is finally deprived of its alcohol in the still (A) and discharged as spent wash.

The strength of the alcohol obtained can be regulated at will. With a strong firing and rapid ebullition in the still (A) the contents of the dephlegmator are heated rapidly and so much that little condensation is effected in it, and only weak alcohol is then obtained. By firing moderately and conducting the distillation more slowly stronger alcohol is obtained; or the same result may be secured by increasing the number of coils in the dephlegmator and increasing its dimensions.

In working this apparatus care has to be taken that the spent wash is not run off until the whole of the alcohol has been extracted. This may be ascertained best by attaching to the still (A) a small ascending worm, connected with a second small descending worm. By opening a cock a small quantity of distillate may be drawn off and tested.

Laugier's apparatus is well adapted for working wine, or other material of a similar nature, which is tolerably uniform in strength, and for producing a spirit of moderate and uniform strength; but it is not well suited for producing strong alcohol, in which case an arrangement of the kind introduced by Cellier-Blumenthal is more

convenient, and can be worked so as to yield spirit having any strength that may be required.

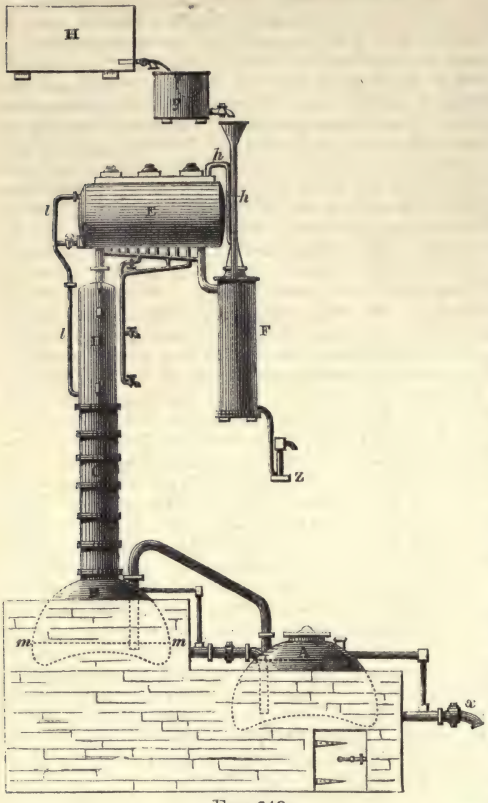


FIG. 649.

Derosne's modification of this apparatus is represented by fig. 649. It consists of two stills, arranged in the same manner as in Laugier's, and the alcoholic vapour escaping from the still (B) rises through the column (C), which contains a series of lenticular discs over which the heated wash flows down from the heater (E) through the pipe (*l l*). Within the column (C) water is condensed from the vapour, and alcohol vaporised from the heated wash, and the vapour passing upwards through the rectifying column (D), and a coil of pipe in the heater (E) is further deprived of water by partial condensation. The extent to which the dehydration of alcohol can be carried in an apparatus of this kind, depends upon the extent of surface exposed in the columns and the other parts.

The apparatus of Cellier-Blumenthal, as improved by Derosne and Dubrunfaut, is used in many of the best spirit works in France. It is represented by fig. 650, and consists of two stills (A B), furnished with steam jackets. The still (A) has a draw-off tap (*a*). To the upper part of the still is fitted a tube (*a''*) by which the vapour is led into the second still (B), which performs the same function as the second still in Laugier's apparatus. The still (B) is furnished with an air-cock (*b''*), and it is connected with the still (A) by the tube (*b*), fitted with a valve. At the top is another tube (*b'*), by which the vapour is led into the bottom of the column (C C), which consists of ten compartments with distillation plates, to be described presently. The tube (D) extending from the dome of the column conducts the vapour into the worm (K'') of the first heater. To the lower end of this worm is connected the receiver (F), in which the uncondensed vapour is separated from the liquid condensed in the worm a pipe being attached to the bottom through which the condensed liquid from the worm, is conveyed into the cooling tube (K'), while the vapour escapes from the upper part of the receiver (F) through a tube (G') connecting it with the worm (H) of the second heater, where the alcohol is condensed and flows, together with any remaining vapour, through the tube (I) to the condenser (K K). The vapour produced in the first heater also passes through the bent tube (*t*) into the tube (I) and into the condenser (K K), where the whole of the distillate is united. The condenser is supplied with cold water from the reservoir (U) through the pipe (V V), and the heated water is discharged through the pipe (X). The worm of the condenser is connected by the pipe (L) with the alcoholometer vessel (M), the overflow of which is immediately above the funnel of the reservoir (N), which is in communication with the storehouse where the spirit is run off into the casks (O O O).

In working the apparatus the condenser (K K) is first filled with cold water, and the tap (*v*) is closed until distillation commences. By opening the cock (P^3) both the heaters (Q H and $R^2 R^3$) are filled, as well as all the diaphragms of the column (C). During this time the air cocks ($a^1 b^2$) are opened. As soon as the still (A) has been two-thirds filled, the air cock (*a'*) is closed, and steam, of from three to five atmo-

spheres' tension, is blown into the jacket of this still. The liquid is thus rapidly made to boil, and the vapour passes through the tube (a^2) into the second still (B), heating the liquid it contains, and driving off a great part of the alcohol in the state of vapour, which passes through the tube (b') into the column (C), and there traverses the layers of liquid upon the diaphragms. The liquor to be distilled flowing downwards

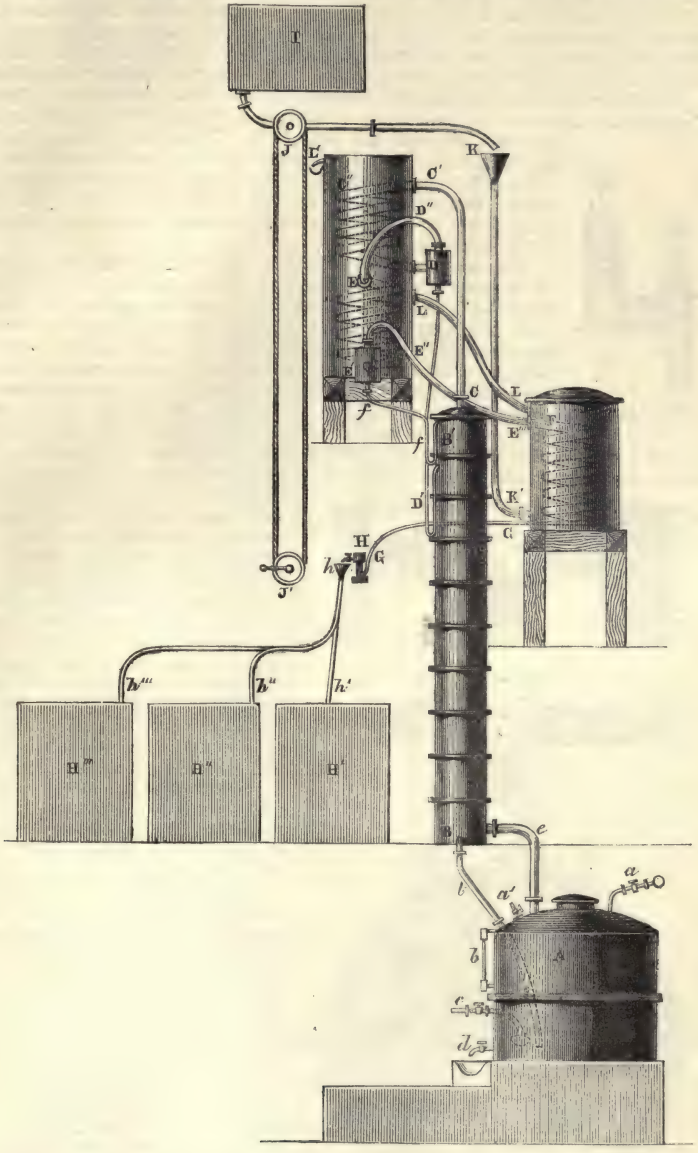


FIG. 650.

in an opposite direction to the vapour is thus gradually deprived of its alcohol as it approaches the lower diaphragms; while, on the contrary, the vapour becomes more alcoholic; since, in proportion as alcohol is vapourised in the diaphragms, there is a corresponding condensation of water-vapour.

During the time requisite for filling the still (B) two-thirds full, the liquid in the

still (A) is completely deprived of alcohol. The spent wash is then run off, and by opening the tap (*b*) the contents of the still (B) are transferred to the still (A), the operation as above described being again repeated. By the action of the column the alcohol is sufficiently concentrated to have a strength suitable for ordinary purposes. A greater concentration may, if necessary, be obtained by making the first heater act as a dephlegmator; and, instead of uniting all the condensed alcoholic liquids, making the portion condensed in the first heater flow on to the upper plate of the column and undergo a further rectification. When the working of this apparatus is to be stopped, the whole of the liquor to be distilled is run out of the reservoir (P); this is then filled with water, and the alcoholic liquor is thus displaced from the several parts of the apparatus.

The liquor to be distilled travels in a contrary direction to the vapour. It is supplied from the reservoir (P) into which it is pumped through the tube (P′) until it overflows through the pipe (P″). The pump represented by fig. 651, consists of a solid plunger working in the barrel (A B) and a pair of ball valves (C D) so arranged that the upward stroke of the plunger raises the liquor through the valve (C), while the down stroke forces it through the valve (D), and the ascending pipe (E) into the reservoir (P) above.

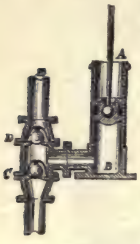


Fig 651.

The tap through which the liquor to be distilled escapes from the reservoir (P) is furnished with an arrangement ($P'''P_4$) by which it can be opened and closed as required to regulate the flow of liquid into the funnel pipe (Q Q) into the second heater, and from there through the pipe (R R) through the first heater, and then through the pipe (S) into the upper part (C′) of the column, where, having become considerably heated in its passage, it is discharged upon the uppermost of the eighteen diaphragms, which have the construction represented in vertical sections by figs. 652 and 653, and in plan by fig. 654. Each of these diaphragms consists of a plate fitted to the sides of the column, and carrying nine hemispherical caps, of which five (*e f g h i*) are shown in the section fig. 652. Beneath these caps are as many holes in the plate having raised collars fitted into them, and projecting upwards into the caps, as shown in the cap (*i*), about half an inch above the level of the edge of the cap. By this arrangement liquid is retained upon the plate to the height of the collars; and, since the edges of the caps dip into this liquid the vapour rising upwards through the holes in the diaphragm into the caps is made to pass through the liquid lying upon the plate.

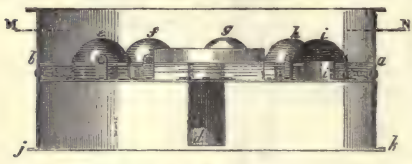


Fig. 652.



Fig. 653.

The level of the liquid upon the plates is kept constant at such a height that it is midway between the upper edges of the raised collars of the tubes and the lower edges of the caps above them. To insure this there is fixed near the centre of the plate a tube (*d*), the upper edge of which is about half an inch lower than the upper edges of the raised collars, and about half an inch higher than the lower edges of the caps. The tube (*d*) extends downwards through the plate, as shown in the drawing, and terminates about three-quarters of an inch above the next following plate (*j k*, fig. 652) beneath. By this arrangement the liquid upon the plate is maintained at the level indicated by the line (*a b*). Anything in excess of this quantity runs away to the plate underneath, while at the same time the openings of the caps are sealed by

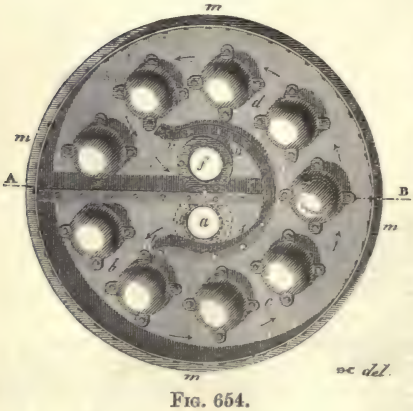


Fig. 654.

the liquid. The ascending vapour can escape only through the raised collars and under the caps, but not through the tube (*d*), because its lower end is closed by the liquid on the plate below. The entire column is made up of ten such diaphragms, fixed one above the other.

In order to keep up a circulation of the liquid upon the several plates, the arrangement represented in the horizontal section (fig. 654) is adopted. To the straight diaphragm (A *r*) is fitted the curved diaphragm (*r s t* on one side, and *r u v* on the other). When liquid flows down from the upper plate through the wide tube at *a*, it takes the course indicated by the arrows in order to reach the tube (*f*) and flows down through it upon the plate below, where similar diaphragms are fixed, and the liquid is made to circulate in a similar manner in the opposite direction.

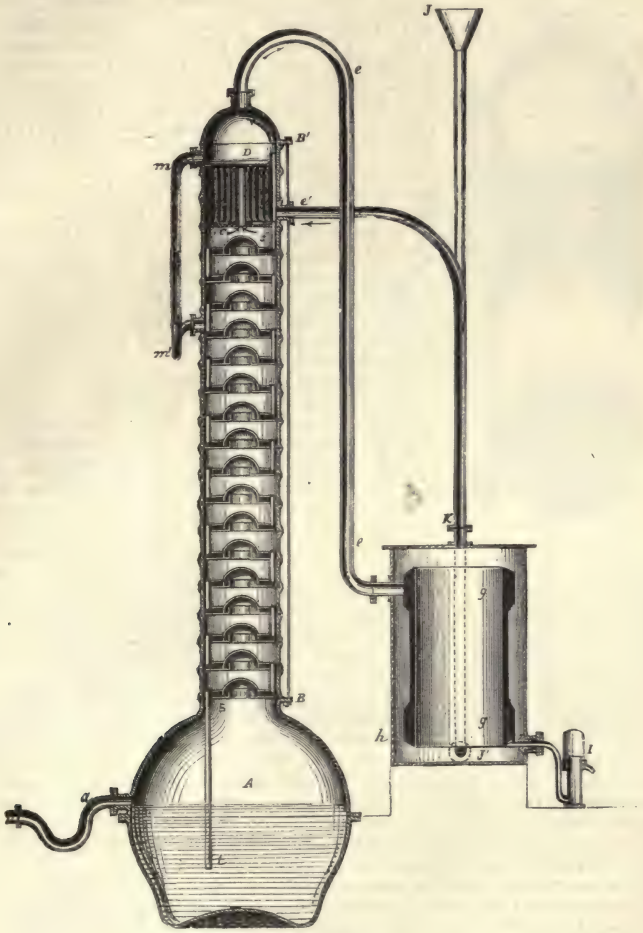


FIG. 656.

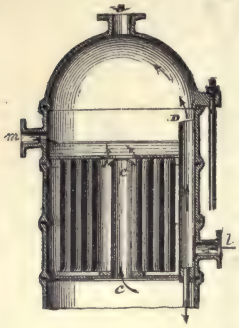
Champonnois' Distilling Apparatus.—The apparatus introduced by Champonnois is essentially a simplification of the Cellier-Blumenthal apparatus, described before. It consists of a still, arranged for an open fire, a column, and a cooling apparatus, and is represented in fig. 656. The still (A) is set over a furnace; it has its bottom bent inwards, in order to present the largest surface possible to the heat of the fire, and at the same time to prevent any deposit, which might form a layer at the bottom were it exposed to the action of the fire.

The column consists of cylindrical rings, the outer edge of each of which has a trough-like depression, in which is laid a caoutchouc ring, and by this means the joints between each ring are closed without screws. The top and bottom rings being provided with flanges (B B'), can be made tight by means of nuts screwed upon the ends of long rods passing through them.

Each ring has a diaphragm with a wide central vapour pipe, covered by a cap, the lower edge of which is toothed so as to distribute the vapour. There is also inserted in each diaphragm a discharge pipe, the upper end of which is one-third of an inch below the vapour pipe, whilst the lower end extends nearly to the next diaphragm.

The peculiarity of this apparatus is the introduction into the top part of the column of a dephlegmator, in which a portion of the vapour is condensed, in order that it may be again rectified in the upper portion of the column. This dephlegmator is shown in fig. 656 at D, and is represented on a larger scale in figs. 657 and 658. It consists of a shallow spiral reservoir with double sides, standing in a vessel filled with the liquid to be distilled. The vapour coming from the topmost division of the column enters the reservoir at *c*, and after circulating in it, passes through a pipe (D) opening above the surface of the liquid, and through *e* to the condenser, whilst the liquor condensed in the dephlegmator, flows through a narrow pipe, bent U-shape at the bottom, into the top division of the column.

Fig. 657.



Instead of the ordinary worm, there is in the condenser a double walled cylinder (*g g*, fig. 656), the walls of which are a small distance apart, so that they form a cylindrical ring surrounded on all sides by the cooling liquid. The alcoholic vapour enters at the upper part of the condenser, is there condensed, and flows off through the alcohometer (I).

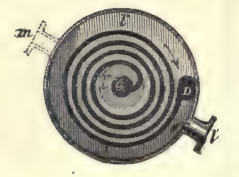


Fig. 658.

In working, the fermented liquor is run from the upper reservoir through the funnel pipe (J) into the outer space of the condenser at J'. When the liquor has filled this space it rises, the lid being hermetically closed, through the pipe (K), and passes into the liquor space of the dephlegmator at *e'*. When this is filled also, the liquor, driven forward by that freshly arriving, falls through a pipe bent first downwards and then upwards (*m m'*) upon the plate of the fourth division of the column, runs through its outflow pipe into the next division, and finally into the still. The liquor is allowed to run until the still (A) is sufficiently full, which is shown by the juice running out through the pipe *a*. The contents of the still are then heated to boiling. The vapour rises into the separate divisions, heating them to the boiling temperature, passes into the dephlegmator, where at first it is completely and afterwards partially condensed, and finally reaches the condenser.

When, by the continued boiling, the contents of the still have been exhausted, a fresh supply of fermented liquor is allowed to flow in at J. This drives the liquid that has become heated in the condenser into the cooling space of the dephlegmator, and from thence into the column, etc. The flow of liquor is then allowed to go on uninterruptedly, and in proportion as this takes place, a corresponding part of the contents of the still (A) runs off through the pipe (*a*), so that the operation is continuous. The firing and the inflow of the fermented liquor have therefore to be so regulated that on the one side a completely exhausted wash is always running off at *a*, and on the other a sufficiently cooled spirit at I.

Stills constructed after the same principle are in the present day coming into more general use in the potato spirit manufacture in Germany. Champonnois' apparatus is so far modified, that the outflow is not continuous, but intermittent, there being two stills heated by steam fixed one above the other, as in the Cellier-Blumenthal apparatus. The fermented mash flows in above, in an uninterrupted stream until the second still is full; the first, which has been meanwhile worked up, is then emptied, and the contents of the second are, by the opening of a valve, transferred into the first. The thicker character of the mash further makes it requisite that the outflow pipes of the different divisions should be proportionally wider, in order to avoid their stopping up. Lastly, the upper rectifying division of the column is considerably increased, and the surface of the dephlegmator enlarged, so as to augment the separation of water by fractional condensation and thus obtain the strongest and purest spirit possible.

Belgian Apparatus.—In the Belgian distilleries, where a comparatively thin corn mash is worked up, as described on p. 924, the apparatus represented in fig. 659 is used. It consists, like Laugier's apparatus, of two retorts (A B), one placed a little higher than the other, which can be heated either over an open fire, or preferably by steam. In the latter case the vapour passes through the pipe (*x*) into the first still, either directly into the liquid, or when steam under pressure is used by circulating through a heating coil. The still has also an exit cock (*y*), an indicator of the height of the liquid (*x*), an air-cock (*v*), and a safety valve (*a*). The steam from the first still (A) passes through the bent pipe (*b*) into the second still (B), and goes from thence into the column (C D), the ten divisions of which are provided with steam pipes covered with caps and with wide discharge pipes. The vapour formed here is carried through the pipe (D′) into the rectifier (E F). E is a comparatively small still in the bottom of which the pipe (D′) ends; it supports a column (F) having a perforated bottom. From thence the vapour passes through another pipe (G) into the dephlegmator (H), the action of which is effected by a coil of pipes provided with a discharge cock at each opening, upon the principle described on p. 902. The liquid here condensed runs back into the column (F). The vapour not condensed in the dephlegmator passes through a pipe (*f g*) into the condenser (S), kept cold by a continuous stream of water, and then through the alcoholometer (U) into the spirit reservoir.

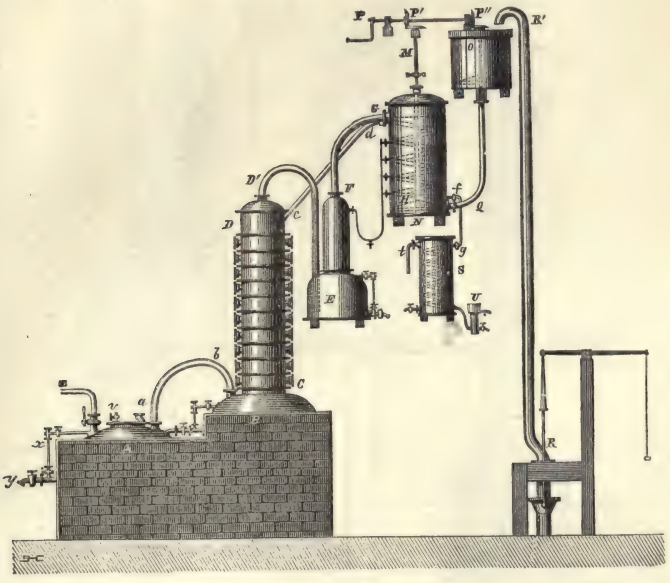


Fig. 659.

The fermented mash is raised by a pump (R) through a pipe (R′) into the mash reservoir (O) in which is a stirrer, worked by a handle (P) and pinion (P″) to prevent the husks from settling. From thence the mash flows through a pipe (Q) entering at the bottom of the dephlegmator, where it is kept thoroughly agitated by the stirrer (M) worked by a pinion (P′); it thus becomes heated, and then passes through a pipe (*d c*) into the top division of the column (E D), and thence from one plate to another, and comes, almost exhausted of spirit, into the second still. The heating is so regulated that the contents of the first still is vapourised in the time required to fill the second. When the first is emptied the contents of the second are run into it. The object of the interposition of the third still (E) with its column (F) is the further rectification of the vapour; at the same time the value of the wash is thereby considerably increased. From this still no back flow of condensed liquid takes place; all the fusel oil, therefore, which was vapourised in the first two stills and in the column (E D) is retained here, and the wash in the first and second stills is thus freed from that constituent, besides being made more concentrated by the retention of water in E.

Savalle's distillatory apparatus (fig. 660) is constructed upon the same principle as

his rectifying apparatus. It consists of a still (A), which supports the column (B), formed of numerous perforated plates. In this case the liquid to be distilled enters from above, and flows down from one plate to another, meeting the steam that passes upwards through the perforations; it is thus heated and, by undergoing distillation, becomes poorer in alcohol as it descends. The vapour escaping at C passes into the preliminary chamber (D), where any liquid carried forward separates and is carried back

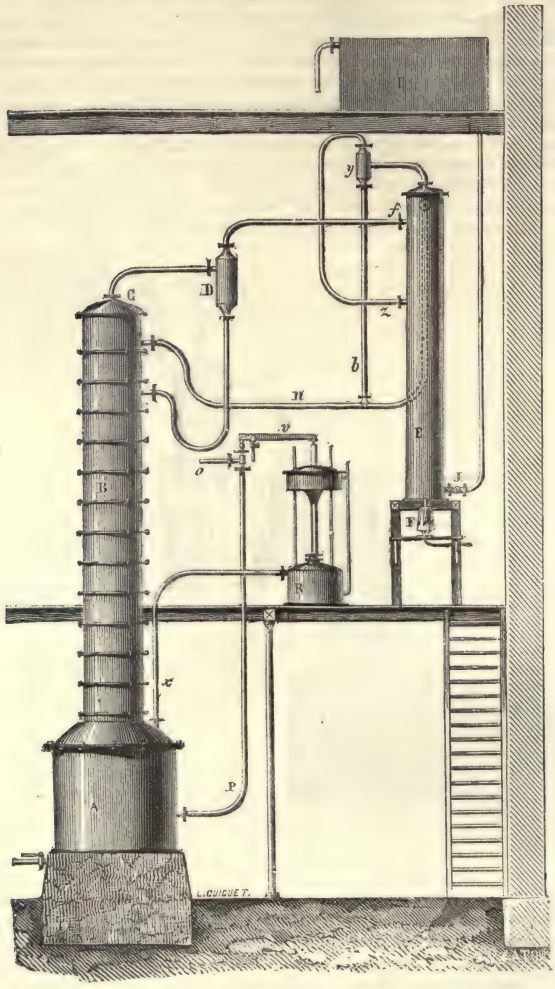


Fig. 660.

by a bent pipe into one of the upper divisions of the column. The vapour goes on through another pipe (*f*) into the condenser (E), and the distillate flows off at F into the alcoholometer vessel, and from thence into the spirit reservoir. The condensation is effected by the fermented liquor, which enters through the pipe (J) at the bottom of the condenser, and as it becomes gradually heated, rises and flows off at the highest point through a bent pipe (*n*) to the top plate of the column. R is the regulator; O the connection with the steam boiler; P the pipe admitting the steam to the heating coil; *x* the pipe connecting the regulator with the upper part of the still.

English Distillatory Apparatus.—As a consequence of the revenue laws existing in this country, the spirit manufacture is limited to a few colossal establishments.

In these the apparatus invented by Coffey is used for the distillation of fermented worts. This apparatus, shown in figs. 661 and 662, consists of two columns, the first (C) being used for distillation and the second (B) for rectification. It is further provided with a dephlegmator (D) and two condensers (E F). The two columns of equal height are constructed of strong cast-iron plates, held together by iron rivets. They are 42 feet high, and rise through four stories of the manufactory. The first column (C) contains thirty-eight copper perforated plates, which are fastened to the sides of the column. The columns are quadrangular, about 20 feet broad by 13½ feet deep. The perforated plates are 4 inches less in width than the interior of the column, leaving a corresponding free space for the overflow of the wort from one plate to another. The plates are fastened alternately to one and then to the other side of the column; by this arrangement part of the wort is caused to traverse the surface of the plate upon which it falls and pours off on the opposite side, and part falls through the per-

FIG. 661.

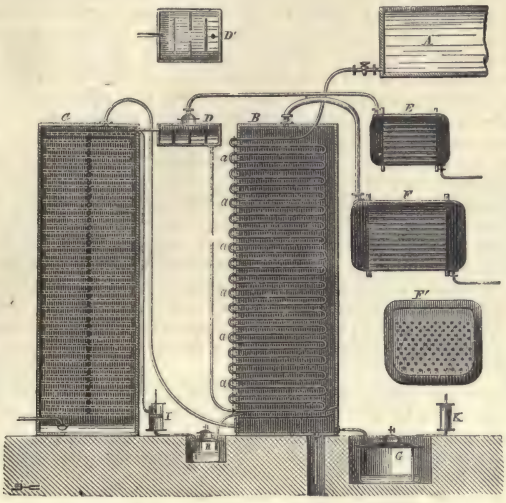


FIG. 662.

forations in a finely divided shower. Between each two plates in the side of the column are manholes which can be shut close, and are used for the purification of the interior of the apparatus.

At the bottom of the first column, the orifice of a steam pipe opens into the liquid. At the top of it is an escape pipe through which the vapour passes into the second column. This is arranged similarly to the column in Savalle's apparatus, but differs from it in that the wort does not flow freely over the plates, but through a capacious pipe, about 6 inches in diameter, bent to and fro (*a a*), the bends of which, in order to facilitate their purification, are carried through the column to the exterior of the apparatus. The wort, coming from the reservoir (A), fills this pipe, flowing down through its windings until it reaches the lowest division of column B. Here it is surrounded by the whole of the vapour coming from the other column (C). This streams from division to division in an opposite direction to the wort, so that the fermented liquor by the time it reaches the bottom becomes strongly heated, whilst the alcoholic vapour as it rises upward from division to division becomes gradually cooled, and by condensation of the aqueous portion continually richer in alcohol.

The heated wort rises from the foot of the second column (B), and after circulating through the chambers of the preliminary vessel (D D'), flows on to the topmost plate of the first column (C). The object of the preliminary vessel is to separate the most volatile portion of the fermented liquid, which has already been converted into vapour by the heat in the second column, and thus to obtain a purer distillate. It is therefore connected by a pipe with a special condenser.

The aqueous liquor condensed from the vapour in the divisions of the second column flows into a small reservoir (H), from whence it is lifted by a pump (J) kept continually going during the distillation, to the top plate of the first column (C).

From the upper end of the second column (B) the vapour, now rich in alcohol,

passes into the tubular condenser (F, shown in section in F'). The condenser is constructed similarly to a locomotive boiler. The vapour enters a first chamber, then into a system of three hundred pipes, each 1¼ in. in diameter, surrounded by a continually renewed stream of cold water, and then flows off perfectly cooled from the last division of the condenser through the alcoholometer stand into the reservoir.

One such apparatus will yield hourly 480 gallons of 58° spirit, or a quantity equivalent to nearly 6,000 gallons of 80° spirit in twenty-four hours.

Rectification of Spirit.—The alcoholic liquid obtained with the foregoing apparatus contains, besides varying quantities of alcohol and water, various, mostly badly smelling, admixtures of other alcohols, ethers, etc. These are separated from the alcohol, and the proportion of water is at the same time reduced, by submitting the liquid to rectification in a suitable apparatus. But since these oils have the property of volatilising readily with the vapour of alcohol, the liquid to be distilled is considerably diluted with water, so that at first a vapour is generated containing proportionately little alcohol and much water, the water being condensed by further running in the apparatus, and the alcohol becoming concentrated. But even with such distillation a fine product is only obtained when the several parts of the distillate are recovered separately; firstly, the portion containing the most volatile constituents being separated, and then that passing over last as after-running. But it is advisable to discontinue the distillation before this after-running comes over, and transfer it to a special vessel, in order to prevent the oils, which distil over in larger quantities towards the end of the operation, from contaminating the sides and interior part of the rectification apparatus; as these bodies collecting there would injure the quality of the following distillate.

The liquor remaining after the rectification, especially when spirit from potatoes, corn, molasses, or grape husks is worked, contains a large quantity of these oils, which having been held in solution by the alcohol, separate from the liquor after the removal of the alcohol in an oily layer, and can then be recovered for use.

Besides glycerin and succinic acid, which occur in all fermented liquors, all kinds of wine contain small quantities of different oils which can be recovered in the rectification. They can also be separated by distillation from the fermented juices of apples, pears, cherries, sugar cane, etc. Only a few of these oils have at present been closely studied.

The best known is the so-called fusel oil, or amylic alcohol, $C_5H_{12}O$, which occurs most abundantly in raw potato spirit, but also in wine and other fermented liquors. In the pure condition, amylic alcohol is an oily liquid, having a specific gravity of 0·818; at a temperature below 23° it solidifies in the crystalline form; it boils at 132°, and has a vapour density of 3·12.

The spirit obtained from wine and wine residues yields during rectification an oily liquid, which consists chiefly of the ethyl ether of œnanthic acid. The free acid corresponds in composition to the formula:

$$\left.\begin{matrix}C_7H_{13}O\\H\end{matrix}\right\}O.$$

The ethyl compound has the formula:

$$\left.\begin{matrix}C_7H_{13}O\\C_2H_5\end{matrix}\right\}O.$$

Both the acid and the ether are, in the pure condition, oily liquids, solidifying at low temperatures, and characterised by a most disagreeable smell. They are insoluble in water, but very soluble in alcohol. The acid boils at 212°, but is then partly decomposed; the ether has a still higher boiling point. Both are lighter than water.

It is not to these compounds that different wines, brandy, rum, or cherry water owe their peculiarly pleasant flavour and aroma; neither is it amylic alcohol alone that gives to potato, beet, and corn spirits their characteristic odour. The bouquet of wines, and the peculiar taste and smell of every fermented liquid, are dependent upon various volatile compounds, many of which are soluble in water, and may be obtained from the vegetable substance yielding the fermented liquid.

The possibility of the separation of all these bodies from the spirit depends upon the varying degrees of heat which are required to convert them into vapour. Alcohol boils at 78°, water at 100°, most of the oils at 130°, 150°, or still higher temperatures; whilst the boiling point of some of the compounds lies far below that of alcohol.

Apparatus for Rectification.—The apparatus at present in use for rectification resembles the Cellier-Blumenthal distillatory apparatus. Such an apparatus is represented in fig. 663. The still (A) has a capacity of from 600 to 1200 gallons and the larger capacity is most advantageous for working. The steam is forced into the still through the pipe (*c*) terminating either in a rose or a coil of pipe. The tap (*d*) serves

to draw off the spent wash. The pipe (*a*) is for the supply of weak spirit. The tap (*a'*) serves either as an air cock, or for testing whether the vapour produced still contains alcohol, and the gauge glass (*b*) shows the level of the liquid. The alcoholic vapour passes from the still through the tube (*e*) into the bottom of the column (B), while the liquid condensed in the column flows back nto the still through the pipe (*t*).

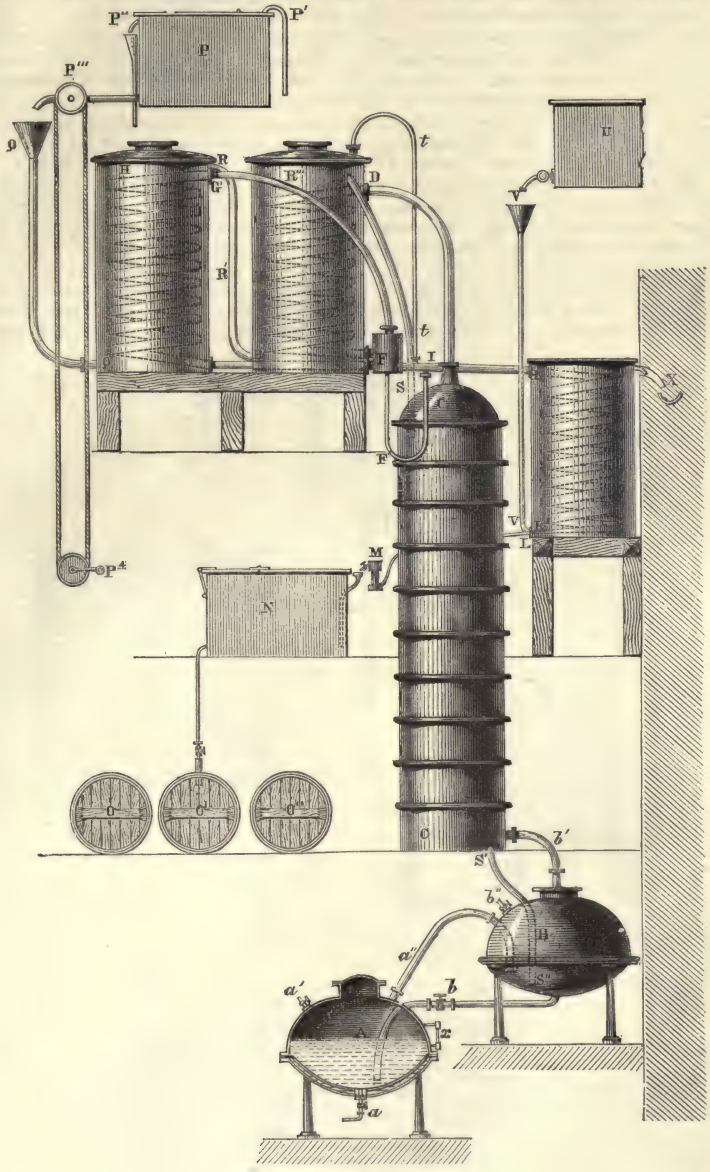


FIG. 663.

The column (B B') consists of ten compartments, with eighteen diaphragms, similar to those described at p. 893. The alcoholic vapour escaping from the uppermost compartment of the column passes through the tube (C C') to the double dephlegmator,

consisting of two worms contained in a cylindrical vessel. The upper worm (C″) terminates in the receiver (D), to the bottom of which is fitted the bent tube (D′), by which the whole of the liquid condensed in the worm (C″) is delivered into one of the upper compartments of the column, where it undergoes further rectification. The upper part of the receiver (D) is connected by the pipe (D″) with the lower worm (E) of the dephlegmator, and thus the whole of the vapour escaping from the upper worm is passed into the lower worm (E), which terminates in a second receiver (E′), where the condensed liquid is run off as before through the tube (*f f*) into the upper compartment of the column, while the alcohol vapour passes through the tube (E′E″) into the worm (F) of the condenser. In this way the liquids condensed in the different parts of the dephlegmator are returned to different parts of the column according to their alcoholic strength. The lower end of the condenser worm is connected by means of the pipe (G G) with the alcoholometer stand (H), from the overflow of which the distillate runs into the funnel tubes (*h h′ h″ h‴*) and into the reservoirs (H H″ H‴).

If it be desired to carry the concentration further, the upper part of the worm in the condenser can be made to act as a dephlegmator, by adopting the arrangement shown in figs. 664 and 665. By means of pipes (E E) fixed at the lowest part of each coil of the worm (D D), the liquor there condensed can be run off through a common pipe (F′). By more or less opening the cocks (F) governing the pipes (E E), it is possible to obtain the spirit of any desired degree of strength. The condensed liquid is then carried back through the pipe (F) into the upper part of the column, in order to undergo a fresh rectification. Cold water is supplied from the pipe (B′), and cock (B″), and passes

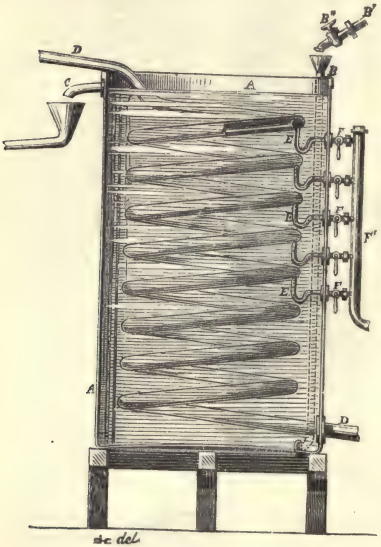


Fig. 664.

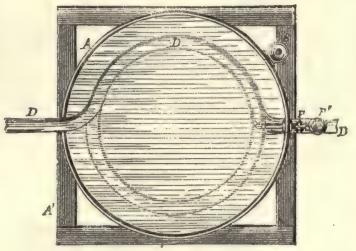


Fig. 665.

down through the pipe (B) into the lower part of the condenser, while the warm water flows off from the pipe (*c*).

The separation and collection of the first runnings, the spirit, and the after runnings are effected by a suitable combination of alcoholometer vessels with a system of pipes, as shown in fig. 666. The lower end of the worm coming from the condenser is provided with a small pipe (A A), through which the air in the apparatus as well as the most volatile and incondensible products are conducted to another pipe opening outside, whilst the liquid runs into the inner cylinder, in which the alcoholometer floats. The distillate rises to the edge of the inner cylinder, raising the alcoholometer more or less according to the amount of alcohol, and thus indicating the nature of the distillate passing at the moment, and it flows over into the outer cylinder (B). This has a discharge pipe, connected with a movable bent copper pipe that can be brought opposite the mouth of any one of the pipes, *b′*, *b″*, or *b‴*, by which the liquid is carried into a special reservoir. In a similar manner several rectifying stills can be connected by the same system of pipes with their corresponding reservoirs,

as shown in figs 667 and 668. The three pipes (A A) lying side by side belong to as many rectifiers, and the air from all escapes into the common pipe (A'). Each pipe passes into a separate alcoholometer vessel (B, C, D). In front of these are the pipes (b, c', d') by which the preliminary runnings can be carried away; (b'', c'', d'') which communicate with the pure spirit reservoir, and (b''', c''', d''') for carrying away the after runnings. When distillation commences in the first still, the alcoholometer vessel of which is at B, the end of the bent portion of the overflow pipe is brought over the opening (b') for carrying off the preliminary runnings. As soon as the alcoholometer shows that pure spirit is passing over, a slight movement of the pipe brings it over the opening (b''). If the second still yields pure spirit at the same time, its alcoholometer vessel (C) is, in a similar way connected with the corresponding opening (c''), and afterwards, when the after runnings begin to flow, with the opening (c'''). In whatever stage therefore the distillation in each still may happen to be, each separate distillate, according to the indications of the alcoholometer, may easily and without the least loss be conducted to the proper reservoir. In each spirit reservoir is placed a float, the counterpoise of which moves on a scale in the immediate neighbourhood of the alcoholometer vessels, so that at any time the heights of the liquid in the separate reservoirs can be easily observed.

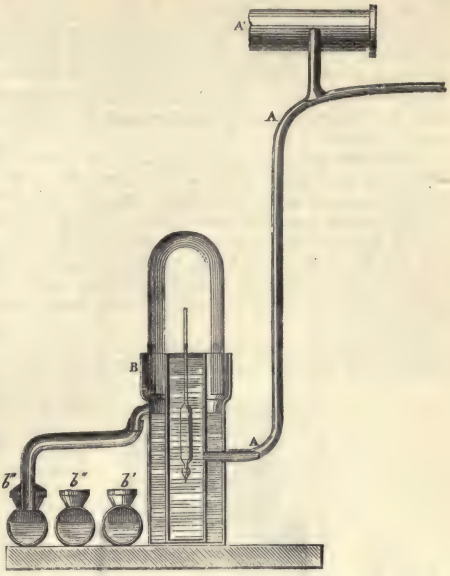
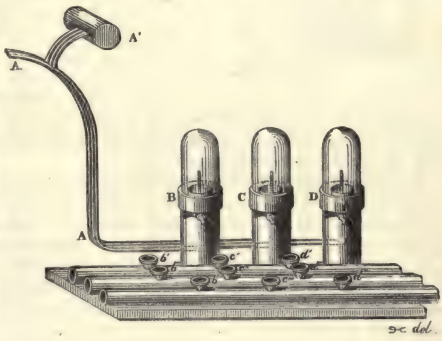


FIG. 666.

In carrying out the rectification the retort is filled with dilute spirit of 49° to 50°, and steam is admitted, the condenser and the dephlegmator being filled with cold water. At first all the vapour condenses in the column and the dephlegmator, and thus fills the separate compartments of the column, the whole of the most volatile constituents, forming the preliminary runnings, collecting in the upper compartments.

FIG. 667.



Gradually the water in the dephlegmator becomes warm, the vapour is no longer completely condensed there, and distillation commences. At the same time the cock through which the condenser is supplied with cold water is opened, and the flow is regulated so that the temperature in the upper part of the dephlegmator shall be 50°. This temperature is 28° below the boiling point of alcohol; an almost complete condensation would therefore be effected here were the

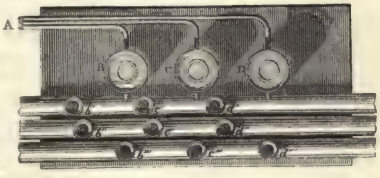


FIG. 668.

alcohol vapour to remain long in contact with the sides of the dephlegmator. But the admission of steam into the still is so regulated that alcohol vapour is abundantly produced, and even after a large quantity has been condensed in the column, it always passes with some rapidity through the dephlegmator, so that although the temperature is lowered it never sinks so far as to cause complete condensation. By the admission of the steam into the still, and of cold water into the dephlegmator, the strength of the spirit can be regulated. In well-arranged distilleries, the steam valves and the water cock are always in the neighbourhood of the alcoholometer vessels, so that by observing the alcoholometers the supply of steam and of water can be suitably regulated.

After the preliminary runnings at the commencement of the distillation have been separated, pure spirit of 96° is first distilled. The spirit is allowed to run off into the proper reservoir until its strength falls to about 90°, or until it no longer possesses the pleasant odour required in fine spirit. Then the after runnings, containing some fusel oil, are kept apart. Frequently this is also divided into two portions, the first, containing the least fusel oil, being used in the manufacture of a common spirit, while the second is again rectified. The operation is ended when a sample of the vapour passed off through a cock into a small worm no longer contains alcohol. The still is then emptied.

In the rectification a certain portion of fusel oil is always vapourised; but the greater part of it is at once condensed in the lower divisions of the column, and flows continuously back into the still, becoming again and again vapourised as long as the rectification lasts. In order to separate this portion of the fusel oil the arrangement shown in fig. 669 has been introduced, by which the liquid coming from the column can be made to flow either back into the still or to the outside. The pipe (D E) coming from the last plate of the column does not open immediately into the still (A), but is first carried through the side of the still to the exterior. Here it branches out into three pipes, which can be closed by the cocks (F G H). One of the branches turns back into the still, so that when the cocks G and H are closed, and F is opened, the liquid coming from the column passes into the still. When F and G are closed and H opened it passes into a reservoir (I) surrounded with cold water, and then by pressure is driven up through the ascending pipe (J). When F and H are closed and G open, everything can be brought directly to the exterior, as, for instance, when it is desired to purify the apparatus, from time to time, or to effect any necessary repairs.

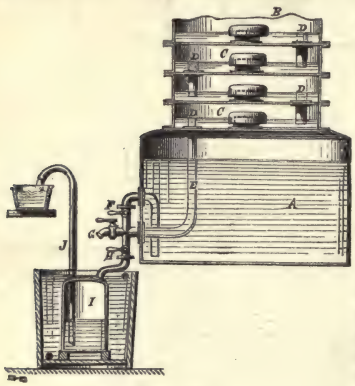


FIG. 669.

Savalle's apparatus for rectifying, represented by fig. 670, consists of the following parts:—A double still (A B), with steam coils; a column (D) formed of a large number of sieve-like perforated plates, upon which the condensed liquid collects, whilst steam rising from below passes through the perforations and through the liquid lying above them, the level of the liquid upon the plates being regulated by escape pipes (*f*), each of which ends in a depression (*g*) on the perforated plate underneath; a cylindrical dephlegmator (E); a cylindrical condenser (F); a cold water reservoir (H); and alcoholometer vessel (I).

In working the apparatus the lower part of the still (A) is filled with dilute raw spirit, and steam is then admitted to the coil of pipes so as to bring the spirit rapidly to the boiling point. The alcoholic vapour rises through a pipe (*b*) into the upper division of the still (B), fills this, and then passes on through another pipe (*e*) into the column. The cock of the water pipe (*b*) is then opened in order to fill the dephlegmator; the vapour rising from the column is there condensed, and flows through the pipe (*k*) back into the column, where it collects upon the perforated plates until they become gradually filled. When this is effected, the inflow of water is regulated by partially closing the cock so that only about two-thirds of the vapour that reaches the dephlegmator is condensed there, and this liquid passing back into the column flows over the perforated plates, continually giving up alcohol to the steam passing through, until when it reaches the bottom of the column it contains little alcohol but much fusel oil. It then either passes through the pipes (*d c*) into the upper division of the still, or is run off from the apparatus altogether. The vapour not condensed in the

dephlegmator goes first into a small chamber where a further small quantity of liquid is separated, and goes into the column together with that from the dephlegmator; the vapour then passes into the condenser (F), where it is completely cooled.

A peculiarity in this apparatus is the automatic regulator (G), by which the admission of steam into the heating coils can be exactly controlled. The construction of the column requires a certain pressure to prevail in the apparatus, which must be

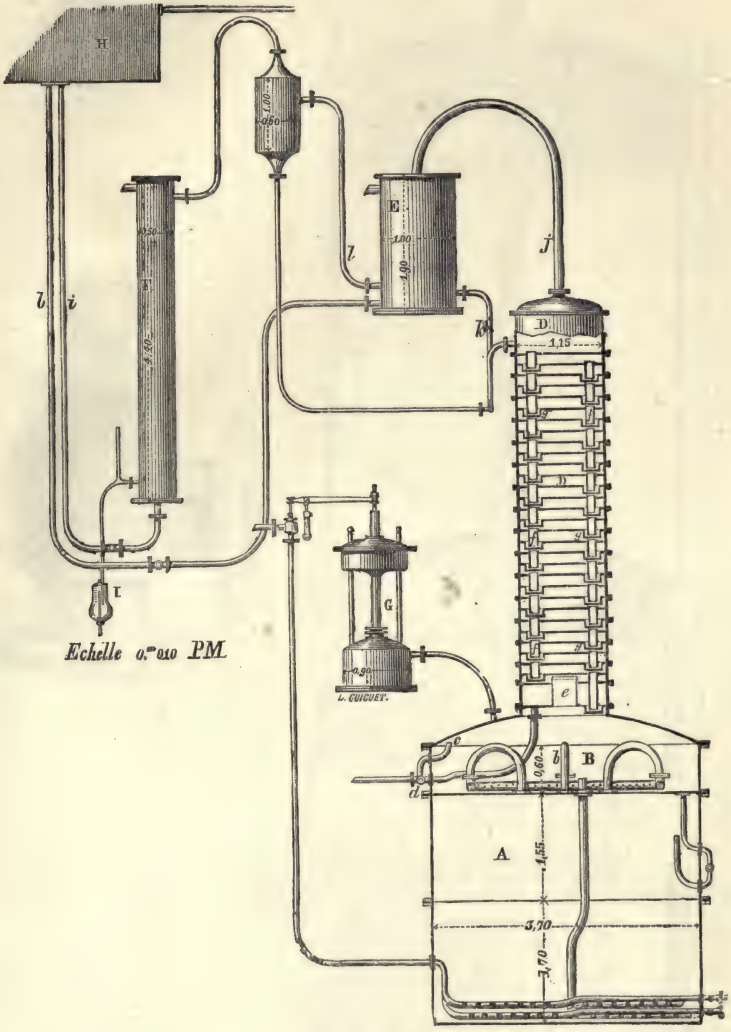


FIG. 670.

obtained before the distillation will proceed. This pressure exercised by the alcoholic vapour is naturally dependent upon the quantity of steam admitted to the heating coils in the still.

In the construction of this regulator Savalle utilises the pressure prevailing in the apparatus to control the admission of the steam. Besides the principal valve in the steam pipe, a second one is inserted, the body of which (fig. 672) is of sufficient width to allow the quantity of steam normally required to pass through when the

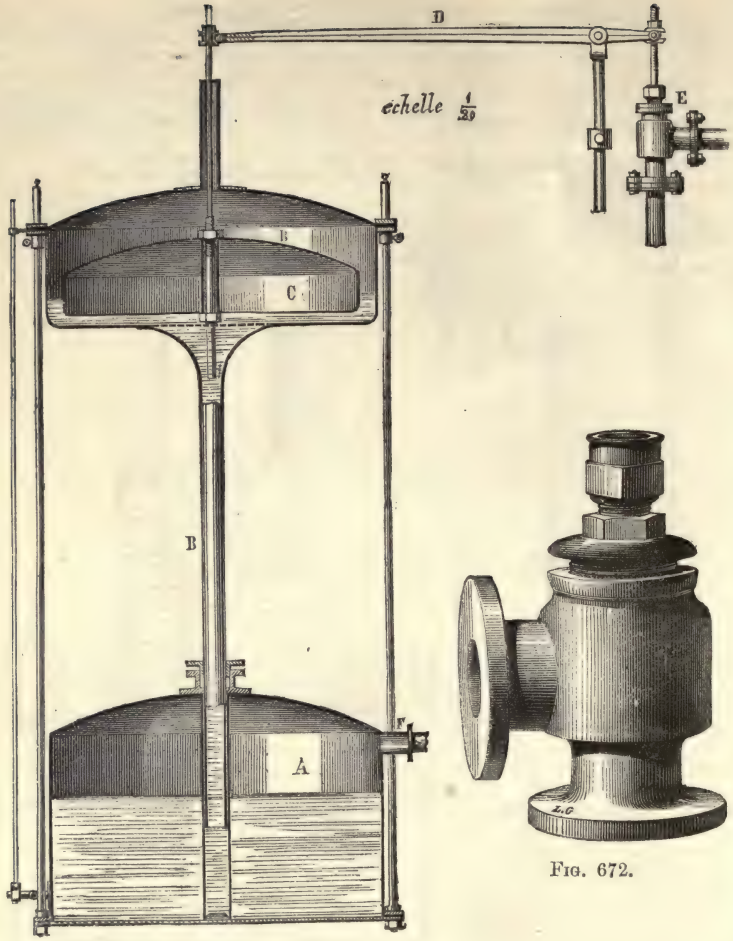


Fig. 671.

Fig. 672.



Fig. 673.

piston (fig. 673) is raised to half its maximum height. It is upon this piston that the regulator (fig. 671) acts. The lower chamber of the regulator (A), partially filled with water, communicates by the pipe (F) with the interior of the second division of the still (fig. 670), so that the pressure prevailing in the interior of the still is communicated to the lower chamber (A) of the regulator, driving a corresponding quantity of water up through an ascending pipe (B) into the upper chamber (B). In this space is a large float (C), which rises and falls with the level of the water in the chamber. At its highest part this float supports a vertical rod, which is fastened to the long arm of a lever (D), whilst the short arm of the lever is connected by means of a screw with the piston of the valve (E).

The action of the regulator is therefore evident. At the commencement of the distillation the piston of the regulating valve is raised to its highest point, and the admission of steam is regulated by the principal valve. As soon as the pressure in the apparatus attains the proper degree, the piston of the regulating valve is connected with the short arm of the lever at such a height as to only half close the opening of the valve. If from any cause the pressure in the apparatus afterwards increases, more water is driven from the lower chamber (A) of the regulator to the upper

one (B), raising the float and with it the long arm of the lever, and depressing the short arm; the supply of steam is thus diminished or brought to a standstill for a time until the normal pressure in the apparatus is restored. If, on the contrary, the pressure in the apparatus is reduced through too great condensation of the vapour, the pressure in the chamber A becomes insufficient to support an equal column of water in the chamber B; a portion of the water flows back into the chamber A; the float sinks, the piston in the regulating valve is raised, and more steam passes in from the boiler.

By means of this regulator, the work of the apparatus can be so equalised that the quantity of distillate per hour does not vary more than a quart. This regularity of production is most difficult to attain, but it is, however the most important part of the rectification. It may be accepted that, of three parts of alcoholic vapour produced in the still, one part should reach the condenser, whilst two parts should be previously condensed and re-worked in the column. Every irregularity in the apparatus or alteration in the inflow of steam for heating, affects the quantity of vapour reaching the condenser. If too much steam be admitted, too much water vapour passes uncondensed through the dephlegmator, and the product is weak, while the fusel oil vapour being insufficiently condensed the distillate is impure. On the other hand, if there be not enough steam in the heating pipes, insufficient alcoholic vapour is produced in the still, and the whole is condensed in the column and the dephlegmator; the flow of spirit is consequently interrupted, and the fuel used during the standstill is wasted. All these inconveniences can be overcome by using the automatic regulator.

Chemical Purification of Raw Spirit.—Many methods have been proposed for the separation or destruction of the foreign constituents of raw spirit by chemical agents. Most frequently the agents suggested have been oxidising substances, such as chloride of lime, potassium chromate, ferric chloride, and cupric salts, which decompose alcohol more readily than the more stable foreign bodies. Compounds are thus produced from the alcohol, many of which are distinguished for their aroma, and the smell of these can cover the fusel oil, although it is not separated. The alkalies—potash, soda, and lime—and potassium carbonate can combine with certain malodorous acids; probably also the ethers of many acids are broken up by combination with the acids, and aldehyd may be partially decomposed; but amylic and similar alcohols are never separated. The only tolerably effective method is filtration of the spirit, diluted to about 50 per cent. strength, through wood charcoal, and this is carried out in all well-conducted German distilleries.

For this purpose a filter battery is used, essentially similar in construction to that used in a sugar refinery (see Sugar). Each separate filter is covered with freshly burnt charcoal, and then filled with the dilute spirit. After passing through the first filter it flows through the others, and is then ready for rectification. When the absorbent action of the charcoal is exhausted, the spirit is allowed to run off at the foot of the filter and steam is admitted, which vapourises any alcohol remaining in the charcoal, together with many other substances absorbed by it, and carries them forward into a condenser connected with the filter. The charcoal is then carbonised in iron retorts and can again be used.

Extraction of Alcohol from Wine, Beer, etc.—When there is an excessive production of wine or cider or the quality is inferior, the alcohol it contains may be profitably extracted and a better price obtained for it in the more portable form of spirit than its natural condition. Beer that is turning sour or is otherwise deteriorated may also be treated in the same way. This is the object of the distillation of wine, which is carried on largely in the south of France, and is there an important branch of industry, though the extent to which it is practised varies from year to year according to the quantity of wine produced.

In the purchase of these liquids, apart from the amount of alcohol they contain, the distiller has to take into consideration the special character of the raw material, especially its aroma or bouquet, as this sometimes imparts to the spirit a special value. Thus, the Montpellier spirit, having a strength of 84°·4, prepared from ordinary wine, is valued at from 3*d.* to 6*d.* per gallon more than well-rectified spirit having a strength of 89°·6, prepared from molasses, grain, or potatoes. Still greater is the difference in value in the finer kinds of brandy and the spirit used in the manufacture of brandy. Thus whilst beet spirit of 90° is of less value than spirit of wine of the same strength, and that from grape residues of less value than either, the brandy of Armagnac and of Cognac of 60° alcoholic strength is worth twice to even six times as much, according to its age, aroma, and delicacy of flavour. In the article on Wine it is pointed out that red, white, or slightly coloured wines can be prepared at will from red grapes, according as the must is allowed to ferment in contact with the skins of the grapes or not. White wines prepared from red grapes are the most esteemed for the brandy manufacture, as they contain in the smallest proportion the constituents of

the skins, which would impart to the brandy prepared from wine containing them an unpleasant flavour, and reduce the value of the spirit prepared from the grape residues. In brandy, as in wine, various volatile substances occur, part of which are probably first formed during the distillation; those of one class are characterised by an unpleasant odour, and originate from the constituents of the skin; those of the other class have an agreeable smell and originate in the fleshy portion of the berries.

In Germany the distillation of wine is not very prevalent, as there is not any over-production of low-priced wines such as occurs in France. In the Rhine provinces occasional experiments have been made to produce Cognac from wine, but at no time to any great extent. In France, however, the case is quite different, for there the distillation of wine yields by far the greater part of the spirit manufactured.

Treatment of Saccharine Materials.—In operating upon saccharine materials, a further process is requisite in order to obtain alcohol: viz. the conversion of the sugar into alcohol by fermentation. This operation is conducted in various ways, either by spontaneous fermentation or by the addition of yeast. The starting point of this operation is almost without exception the yeast produced in brewing, but in the manufacture of spirit, a sufficient supply of brewer's yeast cannot always be obtained, and therefore the manufacturer is under the necessity of producing yeast for the purpose. This is done in two different ways.

According to one method, the saccharine liquid is mixed with enough yeast to set up fermentation, and when this has advanced to a considerable extent, the liquid is divided into two portions, one of which is allowed to continue fermenting while the other is mixed with a fresh quantity of the liquid to be fermented. When the fermentation is sufficiently far advanced in this second portion of liquid, it is divided into two parts and one portion mixed with fresh liquid, while the other is allowed to continue fermenting. This is continued with fresh quantities of the liquid, until the whole is brought into a state of fermentation.

According to the other method, a concentrated saccharine liquid is prepared by infusing malt with warm water; when cold it is mixed with beer yeast, and left until vigorous fermentation has commenced; meanwhile the liquid to be fermented is made ready by the time the fermentation is at its height. The yeast is then divided, and a portion used to set up fermentation in the liquid that is to be fermented, while the rest is preserved for the production of a further supply of yeast by mixing it with a fresh quantity of malt infusion. This is again divided into two portions and used as before.

Both these methods differ only in so far that, in the first mentioned, the yeast intended for setting up the fermentation is produced in the bulk of the liquid to be fermented, while in the other a special liquor must be prepared for the purposes of producing the yeast. The latter method has the disadvantage that since the yeast remains for some time exposed to the atmosphere, acidification takes place by the formation of acetic acid and lactic acid, in consequence of the development of other forms of fermentation besides alcoholic fermentation, and in this way loss of material arises. It is therefore necessary to exercise great care in the production of the yeast. During the time that elapses before it can be mixed with a fresh quantity of malt infusion, it should be kept carefully covered to prevent contact with atmospheric air, and also cooled to a low temperature by enclosing it in sheet-iron boxes, immersed in ice-cold water. If, in spite of these precautions, the yeast shows signs of any considerable formation of acid, which is best ascertained by the taste, it is advisable to throw away the whole and prepare a fresh supply with beer yeast.

In the treatment of beet sugar and molasses, which is now largely carried out, a further point has to be observed. The material is always alkaline, in consequence of the presence of a compound of sugar with alkalies or lime; and since yeast does not cause fermentation in alkaline liquids, the molasses must be mixed with enough acid before the addition of the yeast to neutralise the alkali. Sulphuric acid is generally used for this purpose, and the state of neutralisation is judged of by means of blue litmus paper, which should be only feebly reddened by the liquid. Excess of acid must be equally avoided.

A similar addition of sulphuric acid is made in operating upon beet-root juice, not because it is alkaline, but because it has been found by experience that the fermentation goes on in this material with very much greater regularity when it is feebly acid than when it is neutral. If the addition of acid is omitted, the fermentation goes on very irregularly, the liquid assumes a slimy character, and the evolution of carbonic dioxide causes a violent frothing, by which considerable loss is occasioned. On the contrary, the fermentation proceeds quite uniformly when from one to two parts of sulphuric acid are added to 1000 parts of beet-root juice. The explanation of the influence thus exercised by sulphuric acid has not been ascertained with cer-

tainty, but it has been stated that the acid precipitates a black ferment, though the further examination of this substance has not been undertaken.

In molasses as well as in beet roots the sugar is cane sugar, which is not directly capable of undergoing fermentation. However, by heating cane sugar with a small quantity of sulphuric acid to a temperature of 70°, it can be converted into a mixture of equal molecules of grape sugar and fruit sugar in a very short time, and both these kinds of sugar are susceptible of fermentation. Some manufacturers carry out this operation by heating the acidified solution of molasses up to the boiling point; but this is not necessary, since yeast has the power of converting cane sugar rapidly into grape sugar.

The progress of the fermentation is regulated by the amount of yeast, and by the temperature of the liquid. If it is required to take place rapidly, the saccharine liquid is mixed with yeast at a temperature of about 20° or 22°, and when it is required to take place slowly, a temperature of 17° or 18° is necessary. The quantity of yeast added is also of influence upon the rate of fermentation, but no general rule can be laid down, since it is also affected by a number of other conditions. The temperature of the place where the fermentation is conducted, the extent of surface exposed, the conductibility and radiating capacity of the vessel in which the fermenting liquid is contained, the variations of temperature caused by changes of atmospheric conditions, the quality of the saccharine solution, and its relative susceptibility to fermentation, as well as the quality of the yeast, are all circumstances which, together with others, influence to some extent the fermentation, and must therefore be taken into consideration.

When the fermentation is completed, the liquor is treated in the same manner that has been already described in the case of the distillation of alcoholic liquids.

Fermentation of Fruit.—All kinds of fruit can be made to yield alcoholic beverages, each having a peculiar aroma. One of the most agreeable of these is kirschwasser, the best qualities of which are produced in the Black Forest, but it is also prepared in many districts in France and Switzerland. Its preparation is simple. The sound ripe cherries are plucked and freed from their stalks, and after slightly crushing the entire mass, about one-fourth of the whole is removed in order to crush the stones, and then again placed with the remainder. The kernels contain amygdalin, which by decomposition is converted into oil of bitter almonds, hydrocyanic acid and sugar, the first two imparting to the product a peculiar and agreeable aroma. According to the degree to which it is desired that this aroma should be predominant, the proportion of crushed kernels must be varied, the taste and smell of kirschwasser becoming more intense the larger the proportion of kernels crushed. The pulpy mass passes gradually into fermentation. As soon as this is over the distillation is proceeded with by forcing steam through the pulp, and collecting the distillate as long as it is sufficiently strong. The after running is collected separately, and added to the next quantity of pulp to be distilled.

Manufacture of Alcohol from Sugar Beet.—The production of alcohol from the juice of the beet was first attempted by Dubrunfaut in 1824, but the manufacture was very soon relinquished on account of the low price of spirits at that time. In 1837 a manufactory was established in Valenciennes for the working of beet molasses for alcohol and potassium salts. Since 1845 the beet spirit manufacture in France has increased considerably; many sugar manufactories have been converted into distilleries, and in others arrangements exist for producing spirit or sugar, according as the price of either may make its manufacture the most profitable. For the conversion of a beet sugar manufactory into a distillery only the addition of fermenting vats and distillatory apparatus is necessary, whilst the existing utensils, the beet washers, raspers, juice presses, defecating pans, reservoirs, and piping, all are utilised. By the addition of a column to the vacuum apparatus it can be easily converted into a distillatory apparatus.

The method of procedure, which is subject to many modifications, is in general as follows:—

The cold juice flowing from the press is heated to 20° in the defecation pan, passed into the fermenting vat, and mixed with about 4 lbs. of concentrated sulphuric acid diluted with ten times its weight of water for every 220 gallons of juice. This acidification converts the unfermentable cane sugar into glucose, and also prevents the development of a peculiar ferment which induces a mucous fermentation.

In the first operation fermentation is started by the addition of beer yeast, and the yeast is propagated by proper sowing. For a vat containing about 3,300 gallons of juice 16 to 18 lbs. of yeast are used, carefully distributed through 10 or 12 gallons of water. In cold weather the fermentation is stimulated by warming the juice in the fermenting vat, after the addition of the yeast, to a temperature of 21° to 22°. The fermenting vats, in order to protect the contents from cooling, are closed with covers

provided with a trap door, through which the fermentation can be observed. The progress of the fermentation is controlled by testing with the saccharometer. Immediately after the addition of the yeast to the juice the saccharometer indicates 11°, and the indication sinks gradually until the fermentation is ended, when it is constant at 1° to 2°.

The fermentation lasts from three to four days. By regularly filling two or three vats daily, there will be altogether 8 or 10 vats required, so that one may always be ready for filling and one in reserve.

When the fermentation in the first vat is concluded, the nearly clear contents are drawn off for distillation. The yeast formed during the fermentation lies upon the bottom, and is left in the vat, in order to set up the fermentation in the fresh juice with which the vat is then filled. Besides the fresh yeast, however, there remains also the old decomposed yeast, which favours the collection of a large quantity of foreign ferments. One frequent result of this is an irregular progress of the fermentation. Instead of the liquor entering quickly and regularly into alcoholic fermentation, showing a regular rise in the temperature, there is frequently observed, in consequence of the foreign ferment, only a slight evolution of carbonic anhydride, and a slow rise of temperature, the liquor becoming continually more acid; so that when it is distilled only a small quantity of alcohol is obtained, and the wash contains much acetic acid or lactic acid. It may also happen that the liquor suddenly enters into energetic fermentation, forming a thick scum and foaming over the sides when the vats are not sufficiently capacious.

Whenever an irregularity of this kind takes place the yeast should be completely removed, the vat washed with boiling water, then with milk of lime, and afterwards with pure water, and fresh beer or pressed yeast used for the next lot of juice. It is advisable always to avoid allowing the yeast to collect in the vat for any long time. and to effect a partial renewal of it at each operation.

The wash from the beet roots, being mixed with the pressings, yields a fodder having the same relation to the beet root used as the potato refuse to potatoes. In both cases the relative proportions of the constituents have been rendered more suitable for feeding purposes; the excess of sugar being separated from the beet roots, as some of the starch is from the potatoes, while the whole of the albuminous substances and mineral constituents are retained. The refuse from a beet-root distillery has therefore a very high agricultural value.

The only disadvantage attending its use arises from the large amount of water in the spent wash, which is greater than in the juice of the beet root when in the extraction of the juice water is added as in the manufacture of sugar. This disadvantage may however to some extent be obviated, and at the same time a complete extraction of the juice may be secured by using spent wash instead of water. Further concentration of the juice is effected by using coils or jacketed vessels for the steam used in the distillation, in place of blowing it directly into the stills; and further by attaching to the distillatory apparatus a special rectifier for separating the water condensed, as shown on p. 897.

The extraction of the juice is sometimes effected by a process of diffusion somewhat similar to that practised in the manufacture of sugar from beet root. This method of extracting the juice however may be carried out for the purposes of spirit manufacture with more simple apparatus that involves little cost in its erection. In addition to the machine for cutting up the beet roots, it consists of a series of eight or more wooden vats or tubs with perforated false bottoms. The bottom of each of these vats is connected by means of a wooden pipe with the top of the next succeeding vat. The vats are also fitted with wooden pipes for completely discharging the liquid contents, and with steam pipes, by means of which steam can be blown into the pipes connecting the vats. In carrying out this process, that part of the juice contained in the cells ruptured in cutting up the beet roots is simply washed out, but the far greater part contained in the cells which remain intact can only be obtained by passing through the membrane of the cells by diffusion. The first and the eighth vats of a series, communicating by means of a pipe and a cock, are placed out of communication by closing the cock. About 10 cwts. of beet-root slices are placed in the first vat, which is then filled up with water. The second vat is then filled with slices. While the water is flowing into the first vat, steam is passed in through the pipe by which the first and second vats communicate. The water is thus heated, and comes upon the slices in the second vat almost boiling, and thus disintegrating the cells facilitates the process of diffusion. After some time the third vat is filled with slices, and steam passed into the tube connecting the second vat with the third, while cold water is run into the first vat and the liquid thus displaced from it into the second, where it is heated by steam, passes hot into the third vat, while cold water is again run into the first. In this way the whole of the vats are filled with slices and liquid, fresh water

being always run into the first vat and the liquid heated by a jet of steam every time it comes into contact with fresh slices. When all the vats are filled the contents of the first vat are exhausted. Communication between the first and second vats is cut off, the water run away from the bottom, the exhausted slices removed, and a fresh supply put into the vat. On the other hand, the juice in the eighth vat contains sufficient sugar for fermentation, and it is then drawn off. Fresh water is then run into the second vat so as to drive the contents of the seventh into the eighth, after which the liquid in the eighth vat is heated by steam and driven into the first vat. The second vat is then cleared out and refilled, water being run into the third, and the second then yielding a fermentable liquor. The disadvantage of this method is the loss of the spent wash, which is too bulky to be consumed by such a number of cattle as can conveniently be kept in connection with the works, and it has been in many places superseded by the method introduced by Champonnois, which admits of the consumption of the spent wash and other residues.

By Champonnois's method the beet slices are placed in a vat having a false bottom, and for every ton of beet 4 lbs. of sulphuric acid, previously diluted with thirty times its weight of water, are added, and then 50 gallons of boiling wash poured on. Water is used only at the first stage of the operations; afterwards the spent wash from previous operations is used. After standing an hour the liquor is drawn off and brought into a second vat filled with fresh slices, the first being refilled with fresh wash. The maceration is continued in both vats for another hour, when the liquor is run from the second vat into a third vat containing fresh slices, and that in the first vat is transferred to the second. After being macerated with the third quantity of slices, the liquor, which has been increased about one-fourth in volume by the beet juice it has taken up, has become sufficiently rich in sugar to be passed into one of three fermentation vats. The first vat, the beet in which has already been exhausted with two quantities, is again filled with wash; but this is only left in contact during half an hour, to allow time for a portion of the adherent liquor to drop through the perforated bottom before the residue is removed for fodder. The operation is repeated so that the vat containing the fresh slices is filled with the liquor which has been in contact during an hour with the slices in the next previous vat, whilst the slices in that vat undergo a second maceration with the liquor from the next previous. The liquor from the slices undergoing a third maceration before it is passed into the next vat is heated in a special vessel nearly to boiling, in order to exhaust the beet with which it comes into contact as much as possible. Each quantity of beet slices undergoes consequently three successive exhaustions, in which the greater portion of its sugar is exchanged for the constituents of the wash, and thus a large part of the beet constituents are removed before the residue is used for fodder.

The work can be considerably simplified by connecting the three vats by means of pipes, in such a manner that a pipe passes from below the perforated bottom of one vat over the top of the next. By the introduction of a three-ways cock these pipes can then be used for drawing off the finished liquor. A section of such a cock in connection with the piping is represented in fig. 674. With the position of the cock there shown, the pipes (A and B) between the two vats are connected; but upon turning the cock one-fourth round the perforation (*a b*) connects the channels (A and C). The connection being open between A and C the liquor can be run off entirely; but when it is open between A and B it passes from one vat into the other as soon as the level of the liquid is higher in the first than in the second.

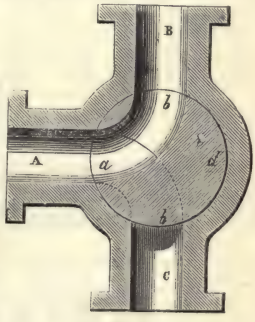


FIG. 674.

The fermentation is so carried on that a proportionally large quantity of continually renewed yeast acts upon the sugar at one time, by which means the most perfect fermentation possible is produced in the shortest time. The juice begins to ferment at a temperature of 16° to 17°, which, as a rule, it attains without further attention, as the wash comes almost boiling on to the slices, and the first liquor drawn off has a temperature of 40° to 50°, which is reduced during the last maceration to the given point. During the fermentation the temperature of the fermenting liquid should not rise above 23° to 25°.

Arrangement of a Beet Spirit Distillery.—Figs. 675 and 676 are plans of a spirit distillery, suited to the operations carried out in the agricultural districts of France, according to the method of Champonnois. Fig. 675 is a ground plan, showing the

shed (A) into which the beet roots are brought through the large door from the pits, in order to be cleansed in the washer (B), and made ready for the slicing machine (C), both of which are set in motion by the horse mill (Q). The beet roots are cut into thin slices and placed in one of the macerating vats (D D), and the exhausted slices

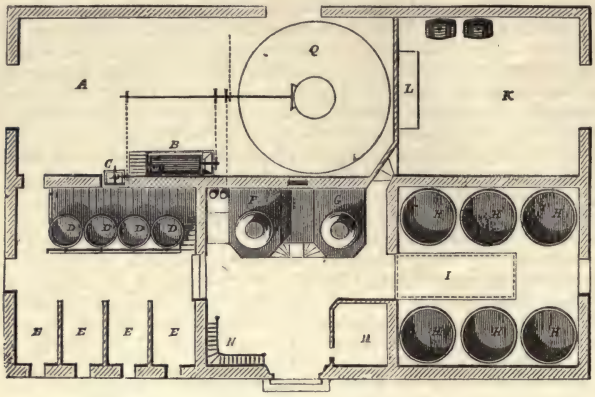


FIG. 675.

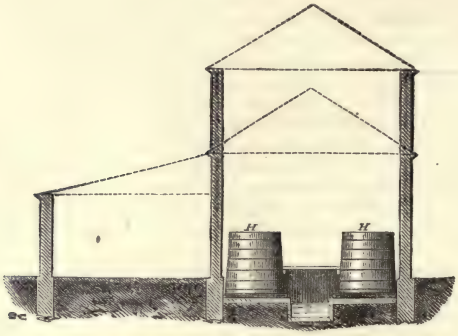


FIG. 676.

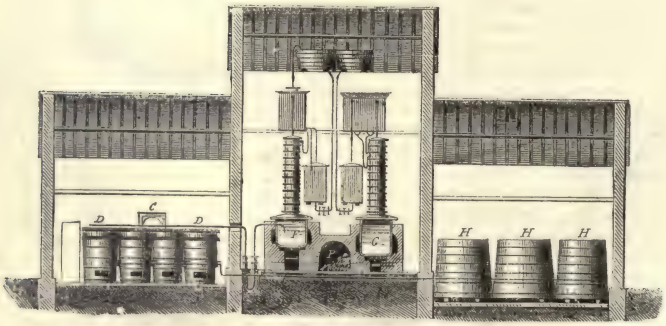


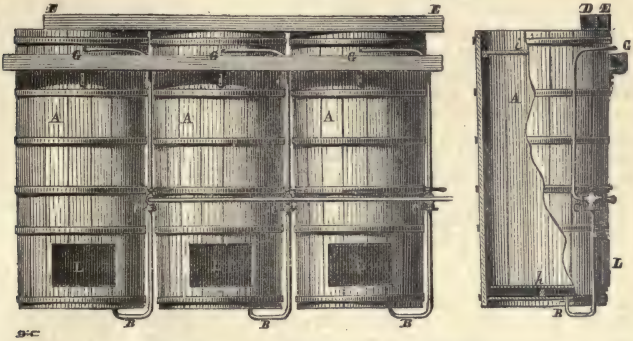
FIG. 677.

are then mixed with coarse fodder in the receivers (E E), and run upon a tramway to the cattle stalls for consumption. The juice obtained by macerating the sliced beet roots with wash, is run first through an open and then through an underground trough to the fermentation vats (H H, figs. 676 and 677). In the middle of the fer-

menting room is a deep reservoir (I, fig. 675), into which the fermented liquor passes from the fermentation vats, and from this it is raised by a pump into the two higher reservoirs above, whence it can flow into the distilling apparatus (F G). The distillate runs into a reservoir (L) in the store-room (K), which is separated by massive walls from all the other rooms in the distillery. Here it is filled into casks ready for transport.

Vertical and horizontal sections of the maceration vats are shown in figs. 678 and 679. In the lower part of these is a false bottom (*h*) perforated with holes, upon which the slices of beet root rest. Above is another shelf (*i*), also perforated, by means of which

FIG. 678.



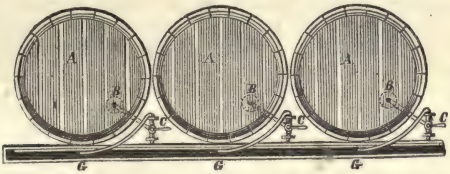


FIG. 679.

the wash and water to be used in the maceration are distributed over the beet root. These liquors are run into the vats from special vessels placed at a higher elevation. The vats are emptied by means of pipes (B C G) opening into the space below the lower false bottom and controlled by a three-ways cock. Through these pipes the liquor rises to the trough (G G), at the end of which is a pump, by which the liquor is raised to the higher trough (D E), and then flows on to the fermentation vats. The exhausted slices are removed from the maceration vats through openings (L L), on a level with the false bottom. During the working, these openings are closed by strong doors fastened by a screw, as shown in figs. 680 and 681. More detailed information as to the method of obtaining the juice has been given under SUGAR.

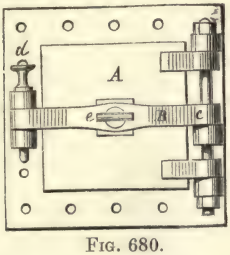


FIG. 680.

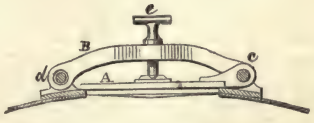


FIG. 681.

The fermenting vats are sufficiently large to contain about 550 gallons. The fermentation is started by running the first yield of 55 gallons of liquor from the maceration vats into the fermentation vat, and adding to it about 10 lbs. of beer yeast suspended in water or in juice. Fermentation commences at once. After

standing an hour another 55 gallons of juice is obtained from the second maceration vat, and this is run into the fermenting liquor. Fresh additions of juice are similarly made every hour until the vat is full.

The full vat is allowed to stand twenty-four hours; a cock is then opened near the bottom, communicating with the second fermentation vat, into which half of the liquor from the first one passes. As each fresh quantity is added hourly from the maceration vat, it distributes itself equally between the two vats and passes into fermentation. Twelve hours after the filling is ended, the principal fermentation is exhausted. The connection between the two vats is then shut off; the liquor in the first vat is allowed to stand for a further twenty-four hours for the after fermentation, and is then ready for distillation; and half of the contents of the second vat are similarly run into a third. Whilst the after fermentation is going on in the first vat, the second and third are being filled with fresh juice, and the liquor in the second vat is then in its turn allowed to stand for the after fermentation. When once the work is in operation, there is thus provided every morning: 1. A vat containing perfectly fermented liquor, which is distilled in the course of the day; 2. Another in which the after fermentation will be completed during the next twenty-four hours; 3. A third, in which fermentation has arrived at the same stage as the next previous one, the contents of which will be divided and mixed with fresh juice.

The progress of the fermentation is examined with the thermometer and saccharometer. The temperature of the liquor rises gradually from 16° or 17° to 22° to 25°, and at this point it remains constant during the first fermentation, and then gradually falls. The saccharometer indication is lower in proportion as the fermentation of the sugar progresses.

Four fermenting vats are always worked together. In emptying the one in which the liquor is ready for distillation, the precaution is taken not to draw off the whole of the liquor, a small quantity—about 100 gallons—being left. During the fermentation, the inactive and exhausted portions of the yeast are deposited at the bottom of the vat together with impurities from the juice. These are now stirred up with the last portion of the liquor, and the whole run off into a special vessel, in order to bring it immediately into the distilling apparatus. This is done because the impurities would otherwise be deposited upon the plates of the column, and contaminate them. Being submitted to continued boiling during the distillation, these substances, in consequence of the amount of albumin they contain, can only increase the value of the residue. They are therefore left in the wash, and when used in the maceration of the slices of beet are retained by them as in a filter. After the separation of these deposits, each fermenting vat undergoes a careful purification before it is again used in order to prevent as far as possible the accumulation of foreign ferments. It is further very advantageous if every evening, after the work is finished, all the maceration vats are emptied and perfectly cleansed, since the liquor remaining in contact with the slices frequently becomes slimy during the night, and then interferes with the normal progress of the fermentation. The liquor last drawn off from the slices, but not yet rich enough in sugar, is left all night in the boiler, in order that in the morning it may be heated and passed boiling on to the fresh slices. This inconvenience is avoided in those establishments where the work is carried on day and night.

If in obtaining the beet juice a larger quantity of wash be used—about double the quantity of the juice to be obtained—the slices can be exhausted at a lower temperature. The re-heating of the juice can thus be dispensed with; or its temperature may even be lowered, and the excess of heat used to warm the already fermented liquor. The liquor thus obtained is less concentrated, but as it contains a smaller quantity of those substances that are dissolved at a high temperature, it is purer, and the fermentation goes on more easily and regularly, and it is not liable to so many accidents through acetic, lactic, and other fermentations. Champonnois has so far modified his method that at present he uses double the quantity of wash at a temperature of 70°. For cooling the wash which comes boiling hot from the distilling apparatus, a cooler is introduced between the condenser and the dephlegmator, which has essentially the construction of the English condenser represented on p. 899. The fermented liquor to be distilled flows first from the reservoir into the condenser of the apparatus, in order that all alcohol vapour may be condensed. Becoming somewhat heated, it passes then into the outer portion of the cooling apparatus, whilst the boiling wash circulates through the worm, by which means the temperature of the wash is reduced to about 70°, while that of the liquor to be distilled is raised to 55° or 60°.

The distillation is carried out with the column and double still apparatus, in such a manner that one still can be emptied every hour, its capacity corresponding exactly with that of one of the maceration vats.

Use of the Residues.—In a working day of ten hours about 4,000 lbs. of exhausted slices are produced. These are at once removed to the cattle stalls and mixed with

oat, rye, or barley straw, or chopped straw, hay or clover, in such proportions as to give three volumes of dry fodder for every volume of wet residue. When a quantity of this has been prepared, it is stored up in large wooden chests or pits with cemented brickwork sides. The wash absorbed by the beet slices moistens the dry substance; it rapidly becomes heated, and fermentation of its constituents takes place. This goes on during thirty-six hours, when the previously hard, dry mass becomes completely softened and uniformly moist, and acquires a pleasant aromatic vinous smell. In this condition the fodder is acceptable to all kinds of cattle.

This fodder has a considerably higher value than the pressings obtained from the sugar factories, because it contains all the nutritive constituents of the beet root, whilst in the sugar factories a large portion passes into the defecation and saturation slime, another portion is absorbed by the animal charcoal, and lastly the principal part goes into the molasses and is thus lost as fodder.

The high value of the refuse adapts this method for agricultural requirements, and it has been widely adopted in France. The spirit manufacture is there, as in the German potato spirit factories, looked upon as an economic means of providing fodder, and the operations are regulated by the requirements of the cattle. As a partial alteration of the sugar has not here the importance it has in the sugar manufacture, the season of work may be extended over a far longer time; usually it lasts from the beginning of October to the beginning of May; consequently, during the whole of the time that fresh fodder is scarce. This use of the beet root has the further advantage that less consideration has to be given to the essential condition of the sugar factories, the highest possible amount of crystallisable sugar and the least possible non-saccharine matter. The beet roots for the distillery can therefore be cultivated with fresh stable manure, and the largest quantity obtained that a given surface will yield.

Leplay Dubrunfaut's Method.—In the year 1854, Dubrunfaut published the observation that beet roots cut into slices can undergo alcoholic fermentation when they are placed in a fermented or fermenting liquid; a maceration and a diffusion process go on simultaneously, the alcohol formed occurring both in the beet and the surrounding liquor. Upon this observation he based a new industry, which was carried out in the following manner:—

At the commencement of the operation a quantity of beet juice is provided, either by pressure or maceration, equal to double the quantity of beet roots to be worked up on the first day. 1,000 parts of juice are mixed with 2 parts of sulphuric acid, heated to 20°, and placed with some yeast in a vat. As soon as the fermentation becomes lively, a large cylinder, made like a sieve of perforated sheet iron, is let down into the liquid, and this is filled with slices of beet, $1\frac{1}{2}$ inch wide and $\frac{1}{8}$ inch thick, previously acidified with 3 parts of sulphuric acid to 1,000 parts of beet. After the introduction of the slices, the temperature of the fermenting liquor must be kept at 20° to 24°.

The fermentation of the juice appears then to be propagated in the inner tissue of the beet, since it is found that after the lapse of twelve to twenty-four hours, the cells contain alcohol and no sugar. But it is quite likely, from what is known of the action of ferments, that this fermentation of the juice within the cell is only an apparent one. Every fermentation requires the direct contact of the sugar with the ferment. But since the fungus cannot penetrate into the separate cells of the beet roots, it is not probable that fermentation takes place within the cell. The more probable explanation is that in the fermenting liquid there is less sugar than in the beet, so that a process of diffusion is set up. The particles of sugar are drawn out from the beet roots and pass into the liquor, where they are at once decomposed by fermentation, so that gradually all the sugar passes out of the cells. On the other hand the alcohol makes its way into the cells, and this process of diffusion goes on until the proportion of alcohol in the cells equals that in the surrounding liquid.

After the fermentation is ended the sieve cylinder is withdrawn, and when the greater part of the liquor has drained off through the perforated bottom of the sieve, the beet slices are submitted to distillation.

For this distillation a special apparatus is used. The beet slices are placed in shallow perforated iron dishes, having an opening through the middle, through which the dishes can be piled one above another upon a movable iron rod. The lowest dish rests upon the foot of the rod; this is filled with fermented beet slices, and then a second empty dish is placed above it and filled, and this is repeated until a pile of dishes, 10 feet high, is formed. The upper part of the iron rod is then hung from a pulley, and swung into a cylinder of the distilling apparatus, about 4 feet wide, the cylinder being then hermetically closed by a cover. In the upper part of the cylinder there is an escape pipe, connected with a rectifier and a condenser, and steam is passed in through a pipe at the lower part so as to heat the beet slices; this converts the alcohol into vapour, which escapes into the rectifier.

Immediately after the removal of the beet slices from the fermenting vat, a fresh cylinder full is sunk into the liquid, and the fermentation can be thus carried on for a period of a month, fresh slices being supplied as needed.

During the fermentation, the volume of the juice that passes out from the beet slices is greater than that of the fermented liquor which is absorbed. At each filling of the distilling apparatus, therefore, sufficient liquor is removed from the fermenting vat to prevent an overflow upon the immersion of a fresh sieve full of beet slices. This liquor is brought into the distilling apparatus together with the fermented slices. Three stills are advantageously used connected with one another, and with the rectifier. At the commencement of the operation they are each filled with freshly fermented beet and a corresponding quantity of juice. Steam is then admitted to the first apparatus, and communication opened with the condenser. At first, and so long as the upper layers act as a dephlegmator to the vapour, a distillate rich in alcohol is obtained; but in proportion as the upper layers become heated, the distillate becomes weaker. The direct communication with the condenser is shut off, and the vapour passes into the second cylinder, where, coming into contact with the cold liquor, the greater part is at first condensed. Gradually the liquor and the lower dishes become heated, and the vapour that is then formed is strong in alcohol and is passed into the condenser.

By this time, the contents of the first cylinder have been completely freed from alcohol. The steam is therefore shut off from it and admitted directly into the second cylinder, which is set in communication with the third. Meanwhile, the first cylinder is being emptied and filled with fresh slices, so that by the time the distillation of the second cylinder is finished, the third can be connected with the freshly filled first cylinder and the operation made continuous.

It is essential for the success of this method, that the presence of all foreign ferments should be avoided. According to experience this is best effected by the addition of sufficient sulphuric acid to represent 2 parts of acid to 1,000 of liquid. In the normal course of the fermentation, the acidity of the juice is always somewhat less than might be expected from the quantity of sulphuric acid added, and Leplay was of opinion that this neutralisation was due to ammonia or some other alkaline substances formed during the fermentation. This, however, is not the case, and it is more probable that the partial neutralisation is due to the decomposition by the sulphuric acid of the pectic salts, which occur in considerable quantity in beet root, with the formation of insoluble pectic acid.

The slices remaining after the fermentation amount to about 40 per cent. of the weight of the beet root used. These form a fodder, containing a large quantity of water, but it can be preserved for a long time pressed down in pits. The residuary liquor is much diluted by the condensed steam, and is not usually used, although it contains all the soluble constituents of the juice except the sugar.

Spirit from the Molasses of the Sugar Factory.—In commerce three kinds of molasses are met with, that from the colonial sugar factories, that from the sugar refineries, and that from the beet-raw sugar factories. Of these, only the last is of importance in the European spirit manufacture. The first is used in the colonies either alone or with an addition of cane juice, and especially that from damaged canes, for conversion into rum by fermentation and distillation. The portion of colonial molasses coming into the European market is, in consequence of its value as a food material, too high in price to be worked for spirit. The refinery molasses is more frequently used for the sophistication of West Indian molasses, and only the most inferior portion of it is used with the raw sugar molasses in the distillery.

In the concentrated condition, as yielded by the sugar factories, molasses has not the power of fermentation; it therefore has to be diluted with water. This is best done by tilting the cask with the bunghole opened over a vessel filled with boiling water. The thick syrup becomes liquefied by the heat and runs into the water, with which it is mixed by stirring with a spatula. After the greater part of the molasses has run out of the cask, steam is passed into the bunghole; and, condensing on the cold sides, liquefies and washes away the syrup still adhering, thus effecting at the same time a purification of the cask.

The hot concentrated solution of molasses is mixed with sufficient cold water to indicate 20° by the saccharometer. Sulphuric acid is then added until any alkalinity due to the presence of sugar lime, alkali, etc., disappears, and the liquor clearly reddens blue litmus paper.

The temperature of the concentrated liquor is regulated so that after the addition of the cold water required it falls to about 22°: in winter one or two degrees higher, in summer as much lower. Fermentation is then induced in the liquor by the addition of the pressed yeast, or in German factories more frequently by malt yeast. The fermentation commences quickly and is recognised by the bursting of small bubbles of carbonic

acid at the sides of the vat; gradually the evolution of carbonic acid spreads over the entire surface and a white scum is formed. If the scum be so strong that the liquor threatens to rise over the side of the vat, water containing a little soft soap in solution is poured over the scum, which generally causes it to collapse, and at the same time the evolution of carbonic acid subsides. During the progress of the fermentation, the temperature of the liquor rises while its density becomes less. The rise of temperature and the saccharometer indications should be observed morning and evening and noted.

The fermentation of the molasses is ended when the scum disappears from the surface, and the evolution of carbonic acid ceases. The distillation should be commenced at once in order to prevent any secondary changes and the formation of acids in the fermented liquor.

The following observations were made in a well-conducted molasses distillery during the progress of a fermentation. The fermenting vat had a diameter of 9½ feet; the inside height was nearly 9½ feet, the height of the liquor (molasses of 20° S.) was 8 feet. The total contents was about 5,750 gallons, representing upwards of 12,600 lbs. of molasses of 75° S. (sp. gr. 1·357), neutralised with sulphuric acid, and 176 lbs. of yeast added:—

	Saccharometer Degrees.	Temperature.
At starting	20°	22·25°
Second day	18°	24°
Third day	12·6°	30°
Fourth day	6·6°	33·75°
Fifth day	5·5°	35°

The fermented liquor yielded 6·8 per cent. of pure alcohol, or about 3 gallons for every 100 lbs. of molasses.

During the fermentation a rise in the temperature of the liquor beyond 36° should be avoided, as at a higher temperature a conversion of the alcohol formed into acetic acid readily takes place. This is best done by commencing at a low temperature. Should the fermentation notwithstanding become so vigorous as to threaten to exceed this temperature, the fermenting liquor can be passed into another vat previously cooled with cold water, or run through a cooling apparatus.

The inconveniences of secondary fermentations may be produced by the use of bad ferment. Besides the alcoholic fermentation, lactic fermentation is set up, and also, by a special ferment, the so-called mucous fermentation, by the latter of which the whole of the liquid is converted into an almost jelly-like mass. Moreover, when putrefying yeast is used, the evolution of carbonic acid is accompanied by red-brown vapours of hyponitrous acid, very irritating to the lungs, and arising from the decomposition of nitrates, which are always present to some extent in molasses.

But care as to the ferment is only a partial remedy against the secondary fermentations; the most absolute cleanliness is requisite in all the vessels, and throughout the whole building. Every fermenting vat after each fermentation should be most carefully purified; every trace of deposit that may be the carrier of foreign ferments should be completely removed; the entire space in which the vats are placed should be regularly cleansed, and provided with a non-porous floor from which all liquids rapidly drain off. Accidents to the fermentation are very frequently referable to neglect in this respect. If, notwithstanding all precautions, the wrong fermentation is induced, nothing can be done but to remove all the ferment, thoroughly purify all the utensils, and commence again with fresh yeast.

Preservation of Yeast.—Many attempts have been made to preserve yeast for a longer time. It has been mixed with concentrated molasses, or, after pressing, dried at a low temperature with an admixture of powdered wood charcoal or starch. These methods are however of very doubtful utility. The death of a considerable portion of the yeast, when kept for some time, cannot be prevented. Also during the drying, unless great care is exercised the yeast is destroyed, whilst thousands of spores of foreign ferments may be carried by the air to the yeast during the operation. The preservation of yeast is however of less importance, because good pressed yeast can be had almost daily in most places, and by the proper treatment of malt yeast the want can always be supplied.

If the recovery of the potash salts contained in the molasses (see before) be combined with the working for spirit, it is desirable that the spent wash should be obtained in as concentrated a condition as possible, in order to lessen the cost of evaporation. This is accomplished by a modification of the distilling apparatus.

The column of the second still of Derosne's apparatus is divided into two parts, and it can then be so worked that only a small portion of the liquor from the condensed vapour flows back into the still, the bulk of it being rectified in a special still.

Such an arrangement is shown in fig. 682. The first still (A) communicates in the ordinary way with the second (B), and this supports a comparatively low column (C), from which the vapour passes through the pipe (D′) into the third still (B′), with its column

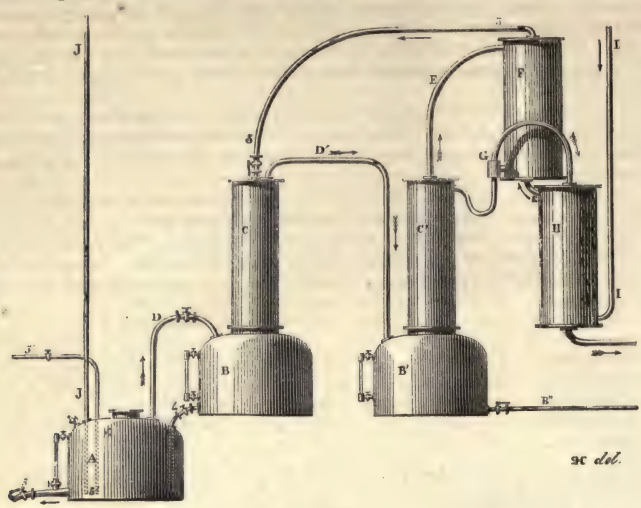


FIG. 682.

(C′), and from thence through the pipe (E) into the dephlegmator (F), and the condenser (H). On the other hand, the liquor to be distilled runs from the reservoir fixed at a higher elevation, into the condenser and thence into the dephlegmator, and becoming thus heated, flows directly into the column (C) of the second still, without passing through the third still (B′) with its column (C′). The liquor which is condensed in the dephlegmator (F) on the contrary runs through a bent pipe (G) into the column (C′), and passes in the opposite direction to the alcoholic vapour into the third still (B′). This still is moderately heated by being placed over the draught from the boiler furnace. From time to time, when it has become nearly filled with alcoholic liquor collected in it, direct steam is admitted and the alcohol is distilled off; the remaining liquor, which, besides water, contains the whole of the fusel oil condensed in the column and in the dephlegmator, is run off through a pipe (B″) at the bottom. Another method is to run off the whole of the condensed liquor at B″, and rectify it in a special apparatus.

TREATMENT OF AMYLACEOUS MATERIALS.—In this case another operation has to be carried out in addition to those already described, viz. the conversion of the starch into fermentable substances. This is done essentially in the way described already, in treating of dextrin and starch sugar (pp. 800 and 806), but with some slight modifications. The conversion of starch takes place under the influence of the diastase in malt, which determines the combination of starch with the elements of water, and its partial conversion into grape sugar according to the equation:

$$\underset{\text{Starch}}{C_6H_{10}O_5} + H_2O = \underset{\text{Grape sugar}}{C_6H_{12}O_6}$$

According to recent observations, which appear to confirm previous statements, the alteration of starch does not seem to be altogether so sharply defined, and it is probable that there is produced with each molecule of grape sugar a molecule of dextrin, so that the change would be expressed by the following equation:

$$\underset{\text{Starch}}{2C_6H_{10}O_5} + H_2O = \underset{\text{Dextrin}}{C_6H_{10}O_5} + \underset{\text{Grape sugar}}{C_6H_{12}O_6}$$

Whether this is strictly correct or not must, however, be determined by further investigation. According to many observations the mode in which the alteration of starch takes place depends essentially upon the temperature, in such a manner that at all temperatures below 65° grape sugar is chiefly produced, while at temperatures approaching 75°, at which diastase is itself altered, chiefly dextrin is formed. Though dextrin is not itself susceptible of fermentation, it does in the presence of sugar take part in the fermentation, perhaps after having been converted into sugar; but in all

cases the presence of a large amount of dextrin has the effect of retarding fermentation, and frequently this substance remains entirely unchanged by it. Consequently, it is above all things essential to conduct the process of saccharification in such a manner that as much sugar as possible may be produced together with the least dextrin; and this object is sought to be attained by keeping the temperature of the liquid in which the starch is being acted upon by diastase from rising above 65°. At the same time it is advisable not to reduce the temperature much below this point, because the conversion of the starch takes place in that case too slowly.

By means of the diastase of malt all kinds of amylaceous materials can be saccharified, provided care be taken to provide for the diastase being brought into contact with the whole of the starch. According to the nature of the particular material to be operated upon with this object, various preparatory operations have therefore to be carried out which will be subsequently described.

Although the spirit manufacturer and the beer brewer make use of diastase for the same purpose, still it has a different significance for each. Malt is the material from which the brewer prepares his beer, but with the spirit manufacturer it is rather the means by which he attains the object of converting into sugar a large quantity of starch over and above that actually contained in the malt itself. The brewer has, however, to provide that the raw material he uses does not introduce into his saccharine liquor substances which would afterwards communicate to the beer an objectionable flavour; and since it is possible for him to employ a proportionately large quantity of diastase to convert into sugar a proportionately small quantity of starch, the malt he employs does not require to contain a large amount of diastase. In the preparation of malt for the brewing of beer, therefore, the germination is stopped as soon as a sufficient amount of diastase has been produced, and the shoots growing out of the grain are carefully separated, because they would communicate to the beer a disagreeable taste. At the same time, by drying and roasting the malt, it is sought to produce certain substances which give to the beer either colour or aroma, and this is done even at the risk of destroying a portion of the diastase in the malt.

None of these considerations have to be taken into account by the spirit manufacturer; in his case it is merely necessary to obtain a material possessing the highest possible sugar-producing capability. This object is secured by allowing the malt to germinate longer; and while the brewer stops the germination as soon as the shoot has attained the same length as the barleycorn itself, the malt used for making spirit is allowed to grow until the shoot is almost twice as long. During the growth of the shoot a large quantity of diastase is formed, not only in the grain but also in the shoot; and therefore the shoots are not removed, but used together with the malted grain. Moreover, since the kiln-drying of malt has the effect of destroying much of the diastase, the spirit manufacturer uses the malt chiefly or almost entirely in the green state. The production of malt should be so arranged that it can always be used in the fresh green condition; or, if it be desirable for any special reason to use kiln-dried malt, it must be remembered above all things that the temperature at which it is dried should be as low as possible so as to prevent the loss of diastase to the utmost.

In conducting the operation of converting the starch into sugar—technically termed the mashing—very different plans are followed, according to the nature of the material operated upon and the custom of different localities. In England, for example, this operation is conducted exactly in the same manner that the beer brewer makes his infusion of malt. When the formation of sugar is completed the clear wort is drawn off, the grains are washed out with water, and the wort is set to ferment. In Germany a simpler procedure is adopted, and the entire liquid is fermented, together with the grain, whatever the nature of the material operated upon. The apparatus used for this purpose is essentially the same as that employed by the beer brewer, in preparing wort (see p. 946), and the only difference is that the mash tuns have no false bottom for the separation of the grains.

When the formation of sugar is at an end, it is above all things requisite to cool the mash as rapidly as possible, and bring it to the temperature suitable for the fermentation, because when the cooling takes place slowly lactic fermentation is apt to take place. For effecting this object the same kind of apparatus is used that the brewer employs for cooling wort, as subsequently described under the head of 'Beer Brewing' (see p. 952); but while the brewer requires to clear his wort while it is being cooled, the spirit manufacturer does not need to do this, and he is able therefore to have recourse to other means by which the cooling of the mash is very much more rapidly effected.

In places where there is abundance of water, and it can be obtained with little cost for use in the works, it may be advantageously used for cooling the mash. For this purpose the apparatus represented by fig. 683 may be employed.

It is constructed so that the liquid to be cooled is made to pass through very narrow passages, while a stream of cold water is made to flow through similar adjoining passages in such a manner as to lower the temperature of the hot liquor. In the apparatus represented in the drawing, cold water is introduced through the funnel (*a*) and after passing through the channels escapes through the discharge pipe (*d*). The hot liquor is introduced through the funnel (*f*) and escapes through the discharge pipe (*i*). Various arrangements of this kind are in use for this purpose.

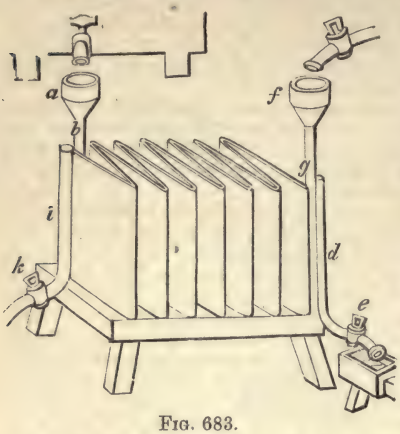


FIG. 683.

The cooling apparatus most generally employed, and that which is in most cases the best suited for the purpose, consists of a shallow round vat made of cast-iron plates, the joints of which are made tight by caoutchouc strips, and held together by screw bolts. In the centre of the vat is a vertical shaft carrying two horizontal arms, upon which a number of iron blades are fixed. The shaft is driven by a belt and made to rotate slowly, so that the mash is stirred up in all directions by the iron blades, and fresh portions are constantly brought into contact with the air, and in this way the radiation of heat, as well as the evaporation of water, are very much facilitated. To promote the cooling by these means still further care is taken to ensure constant renewal of the air surrounding the vat, by fixing over the vertical shaft a second hollow wheel which carries, immediately above the arms of the other, two fans set at an angle. This hollow wheel moves in the opposite direction to the other, and is driven at twice the speed. The fans drive the air before them against the circulating mash, and in this way, by using air alone, the mass is sufficiently cooled.

A more efficient apparatus than that just described is the cooler constructed by Siemens. It consists of a vertical iron cylinder in the axis of which is fitted a revolving wheel which carries a number of horizontal iron discs, and between each pair of these discs there is a ring-shaped projection upon the side of the cylinder. During the operation the wheel is driven at the rate of 600 to 800 revolutions per minute. The hot mash flows through a tube upon the uppermost disc revolving with the wheel, and is thus driven by centifrugal force against the side of the cylinder, collects there, and flows along the ring-shaped projection downwards to the second disc, where it is again forced against the side of the cylinder; then flows over the following ring-shaped projection to the third disc, and so on until it arrives at the foot of the cylinder, where it comes into contact with a strong blast of air forced against it by a fan fixed to the upper part of the wheel that drives the air out of the cylinder with great force, so that, since there is no other opening for the access of air, the air at the foot of the cylinder is made to flow on with the same velocity. Therefore, while the mash is spread out in thin layers upon the several discs, fresh air passes with great velocity against its surface, and thus abstracts the heat so completely that in a very short space of time the mash acquires a temperature several degrees below that of the surrounding atmosphere.

It has recently been the practice to make frequent use of tubular coolers constructed on the same principle as Liebig's condenser. An inclined tube, which, for the sake of saving space, is bent several times backwards and forwards, is surrounded throughout its entire length with a second wider tube. The hot mash is made to flow along the inner tube in such a way that it rises gradually in the tube until it fills it and flows out at the upper end. Through the outer tube cold water is passed in a constant stream, and in a direction opposite to the mash. The heat is thus transferred from the mash to the water in the outer tube, and, according to the rate at which the mash and water are made to flow through the tubes, a proportionate degree of cooling is obtained, together with the advantage that by this means of cooling the mash is kept out of contact with atmospheric air while it is being cooled.

Lastly, there is another kind of cooling apparatus to be mentioned which is fitted in the mashing tun itself. To the stirring apparatus is attached a long tube extending from the upper part of the mash tun to the bottom, then bending upwards and downwards several times, and terminating at the one end in a pan and at the other

end over an open gutter outside the mash tun. When the mashing process is finished, cold water is run into the pan so that it flows along the whole length of the tube and escapes heated into the gutter outside. Since the tube, together with the pan, is fixed to the wheel-work, it can be kept in motion while the water is flowing through it, and the cold water is thus brought everywhere into contact with the hot mash. This apparatus has the advantage that it does away with the necessity for a separate cooling vat; but, on the other hand, it has the disadvantage that during the time required for cooling, the mashing tun cannot be used, and not only has the mash to be cooled with water, but also the entire apparatus. On account of the interruption thus caused in the working, this method of cooling the mash is less suitable for large works than for small ones.

Potato Spirit.—In the German spirit industry the potato is by far the most important raw material. In order to make use of the refuse as fodder, which is specially useful for fat and milk cattle, and to supply it to the farm at the lowest price, the spirit manufacture has there become exclusively an agricultural business.

The potatoes are first purified in the potato washer described under 'Starch' (p. 764). In order to expose the starch to the action of malt diastase in the subsequent saccharification it is necessary that the cells in which it is enclosed should be ruptured. By boiling the potatoes, the starch in the cells is caused to swell until the cell membranes are stretched to the maximum of their elasticity. If the cells in this state are subjected to pressure, the cell membranes burst and the starch is set free, swollen and in a condition specially favourable for the formation of sugar.

The boiling of the potatoes is carried out in tall narrow cylinders, hermetically closed, with the exception of an opening for the escape of condensed water. When the cylinder is filled, steam is admitted to the lower part, which coming into contact with the cold potatoes, is at first condensed, but gradually heats the entire mass until the potatoes are sufficiently cooked. This is ascertained by testing some of the potatoes lying in the upper part of the cylinder with an iron rod. The softened potatoes are then allowed to fall through an opening in the steaming cylinder, and roll along an inclined surface and between two heavy smooth rotating iron rollers, where they are crushed, after which they fall as a mealy mass into the mash tub placed beneath the rollers. This already contains malt, stirred up in a little cold or lukewarm water, in the proportion of 1 part of the best green malt to 15 or 16 parts of potatoes to be worked, and the mixture is kept in constant motion by a stirring apparatus. As the potatoes fall almost boiling into the malt liquor its temperature soon rises, and this accelerates the process of saccharification. Solution of the starch is immediately observable: the mash becomes continually thinner through the setting free of the water of the cell juice, whilst the swollen starch is converted into sugar. When the entire contents of the steaming cylinder have reached the mash tub, the temperature of the mash will be from 50° to 60°, or that most favourable to the formation of sugar. This temperature is ensured by more or less heating the water in which the malt is first stirred. In the colder parts of the year lukewarm water is used, but in hot weather the coldest water possible is used. The principal point to be kept in view is that the temperature of the mash shall not rise above 65°, because above this the action of the diastase is affected, so that a larger quantity of dextrin is formed, and above 75° the diastase is destroyed. Should the temperature of 60° not be reached, the stirrer is set in motion more rapidly and a little steam is admitted, by which the proper degree of heat is rapidly and certainly attained.

During the crushing of the potatoes the stirrer is kept continually in motion, so as to mix thoroughly the whole of the potato mass with the malt liquor. After all the potatoes have come into the mash tub, the stirrer is stopped, the mash tub is well covered up, and the saccharification is allowed to go on quietly for an hour. The stirrer is then again set in motion, and kept working vigorously for an hour or an hour and a half. This has for its object the thorough mixture of the entire contents of the mash tub, and by the bursting of any still unruptured cell membranes to set free the enclosed starch and to bring it into contact with the diastase. About two and a half hours after the introduction of the potatoes the mashing process may be considered ended. A drop of the mash liquid, after cooling, should not become blue when mixed with solution of iodine, indicating that no more dissolved starch remains undecomposed. The finished mash can then at once be cooled.

This method of crushing the boiled potatoes has the disadvantage that it is not possible to rupture all the cell membranes enclosing the starch, so that a corresponding quantity of starch is kept from the action of the diastase. When this is the case, even in the best managed distilleries the full yield of alcohol that might be expected from the quantity of starch used can never be obtained.

This disadvantage appears to be completely overcome by a new method introduced by Hollefreund. It consists in first steaming the potatoes under very high pressure,

and then suddenly, by the blowing off of the steam and the production of a vacuum, bringing them to the mashing temperature, when they are crushed by a stirrer. The apparatus used is a fixed strong sheet-iron cylinder, through the axis of which passes a revolving shaft provided with arms. Above there is a manhole which can be hermetically closed, through which the cylinder can be filled with potatoes, and the cylinder is connected with a steam boiler by one pipe, and with a condenser and air pump by another; there is also a pipe for the introduction of the malt. The temperature and pressure in the apparatus are shown by a thermometer and a manometer. When the cylinder has been filled with potatoes steam is admitted, until the pressure corresponds to a temperature of 125° to 130°. After about forty minutes the stirrer is set in motion, and for about twenty minutes makes from 44 to 48 revolutions per minute. The connection with the steam boiler is then shut off, the steam present in the cylinder is allowed to blow off, and connection is made with the condenser and the air pump. In the vacuum a sudden and violent development of vapour takes place in the interior of each cell through which the membranes are burst open from within. This development of vapour causes a very rapid lowering of the temperature, so that in about twenty minutes it falls to the mashing temperature of 65°. Malt stirred up in a small quantity of water is then admitted, in the proportion of 175 parts of green malt to 2,500 parts of potatoes, and the stirrer is again set in motion, the ordinary atmospheric pressure being restored by the opening of an air valve. The saccharification proceeds very rapidly in the completely disintegrated potato mass; it commences almost immediately, as can be observed in the liquefaction of the mass, and is completed in about fifteen or twenty minutes. The mash so obtained differs essentially from the mash obtained by the ordinary treatment. In the latter can always be seen a quantity of potato fragments that have escaped the action of the crushing rollers, and there can be detected by chemical examination a not inconsiderable quantity of undecomposed starch. The mash obtained by Hollefreund's method is, on the contrary, perfectly homogeneous; only the husks of the malt and the broken potato skins float about in it, whilst the quantity of undecomposed starch is reduced to a minimum. It is therefore evident that from an equal quantity of material a higher yield of spirits is obtained. Moreover, when, as in Germany, the volume of the fermenting mash is the object of taxation, the more perfect saccharification must result in a saving of duty. The only disadvantage presented by this method is that the cost of the apparatus and the amount of power required to work it are somewhat higher than for the ordinary method. But the advantage gained amply covers the increased capital used.

The fermentation of potato mash is almost exclusively effected by artificial yeast. This is prepared by steeping in water in special vessels, at a temperature of 65° to 70°, a mixture of potatoes with 2 or 3 per cent. of dried malt or green malt, or a mixture of the two, or with an addition of unmalted grain. The mixture is usually left to cool to the fermentation temperature, 18° to 22°, and then pressed yeast or common beer yeast is added. During the cooling a considerable quantity of lactic acid is produced, which in the opinion of most distillers is of advantage, inasmuch as a larger quantity of gluten is dissolved from the malt, and more material is thus provided for the formation of the yeast. If, however, the presence of an acid be required for this purpose, it cannot be obtained in a more disadvantageous manner than by the cultivation of the lactic ferment in a substance that is to be used for the manufacture of the alcoholic yeast, as the lactic ferment would be afterwards added with it to the mash. It is far preferable that the mixture should be cooled rapidly by placing it in vessels filled with iced water, and the necessary acid supplied by adding a small quantity of phosphoric acid. Pure phosphoric acid need not be used, but acid calcium phosphate, the so-called superphosphate, may be added in the proportion of 1 to 2 per cent. of the yeast materials.

When this mixture is in full fermentation it is thoroughly mixed by stirring, and the greater part of it is removed for adding to the mash. The remainder, the mother yeast, is kept for use, instead of yeast, in making the next lot.

The preparation of the artificial yeast has to be so regulated that the time at which it enters upon the fullest fermentation always corresponds with the time when the mash has finished cooling and is ready to be run into the fermenting vats.

Respecting the preparation of artificial yeast many contradictory opinions exist, almost every manufacturer having a special method. But there is really no mystery in the preparation of artificial yeast, and it can be produced from the most diverse materials, if only the conditions that govern the life of the yeast plant be kept in view.

The fermentation begins almost immediately after the addition of the yeast, and a light white scum of bubbles of carbonic acid forms upon the surface. As it increases the potato skins and refuse contained in the liquid rise to the top, and form a covering that is soon in active movement. The carbonic acid collecting beneath it bursts

through, and when the fermentation is in full operation the action is so violent that portions of the mass are spirted upwards a distance of 2 or 3 feet. At the same time the temperature of the liquid rises considerably. After a time the fermentation slackens; the carbonic acid is evolved more slowly, and finally ceases to be noticeable; the scum lies quietly above the still slowly fermenting liquid, and the temperature falls. The fermentation is then considered to be ended. The time required for this operation is to some extent under control. At a high temperature, and with a large quantity of yeast, the fermentation can be completed in twenty-four hours; but there is then a danger that the fermentation may become so violent that the whole of the liquid froths up and runs over. Usually the fermentation is so managed that it is completed in three days, being carried on at a low temperature and with the addition of a small quantity of good ferment.

Immediately after the fermentation is ended the distillation is proceeded with, in order to avoid as much as possible any formation of acetic acid.

Corn Spirit.—The working of grain—barley, rye, wheat, oats, or maize—is essentially similar to that of potatoes, certain modifications being required to suit the external characters of the materials. In order to expose the starch contained in the grain it requires to be crushed, but with the exception of maize it is not necessary to grind it into flour. A mill is therefore used which only breaks the outer husk and crushes the grain. Maize must be ground to a fine flour, because in it the layers of starch grains are so compact that they are not otherwise sufficiently exposed to the action of the diastase. The crushed grain is placed with the malt in the vats, about 1 part of green malt to 6 of groats, and first mixed with a little warm water by vigorous stirring with a mechanical arrangement. As soon as the mass has become uniform hot water is admitted, until the temperature of the entire mixture reaches 60° to 65°. The proportion of corn and water is so regulated that there are not more than 3 or $3\frac{1}{2}$ parts of water to 1 part of dry substance, otherwise too great a volume of liquid would be produced. If the water is not sufficient to bring the liquid to the proper mashing temperature, a little steam is admitted, the heat of which easily raises it to the desired point. The saccharification proceeds in the same manner as in the mashing of potatoes. In maize a further preparation is requisite to render saccharification perfect. This consists in boiling the meal with water before the addition of the malt, until the granules are completely softened. The boiling liquid is then cooled to the mashing temperature of 60°, in order to prevent the destruction of diastase, and this is usually done by bringing the boiled mass into the cooling galley. The disintegration and working of maize might be much facilitated by using Hollefreund's apparatus. The further treatment is essentially the same as that of the potato mash.

The yield of alcohol from these various materials is dependent upon the amount of starch they contain; but as this varies, and since the manner of treatment during the manufacture has great influence, no general rule with respect to it can be laid down. Pure starch yields, under the most favourable conditions, half its weight of alcohol; but this yield is never obtained in practice. It may be assumed that on the average only about 75 per cent. of the calculated amount of alcohol is obtained. By Hollefreund's method the yield is better, and can without difficulty be brought up to 90 per cent. According to Payen, 100 kilos of wheat groat yield on the average 29 to 30 litres of 95 per cent. alcohol; rye yields 27 to 28; barley, oats, buckwheat, and maize yield 20 to 25; and rice 32 to 36 litres. This small yield from maize, in proportion to the amount of starch it contains, is doubtless due to very badly conducted manufacture.

In the manufacture of spirit from wheat, the grain is mixed with 15 per cent. of malt suspended in 500 parts of water, and heated gradually to 72°. After standing four hours the wort is drawn off, and a second infusion of water at 50° is made. The two worts are united, cooled to 20°, and after they have been mixed with one-third or one-fourth of the residue from the previous distillation, beer yeast is added. By the addition of this residue fermentation is facilitated. A third infusion is made from the husks with water at 70°, and this weak wort is used instead of water in the next mashing.

In England a mixture of 10 parts of dry malt, 80 parts of barley groats, and 10 parts of oat groats are mashed with the water in the mashing machine in such a way that the resulting wort, after fermentation, shall contain 10 per cent. of its volume of 58 per cent. spirit. The wort is cooled in shallow cooling troughs, or in tubular coolers, the pipes of which are arranged like the boiler pipes of a locomotive, and for easy purification are constructed of copper. The exhausted husks or grains are used for feeding cattle. For the fermentation only clear wort is used. The fermentation tanks hold 40,000 gallons, and fermentation lasts six or seven days. No yeast is manufactured, as this can be purchased more cheaply from the brewer. In the

English breweries a considerable excess of yeast is produced, and on account of the brown colour, communicated to it by the strongly dried malt of the porter brewery, it is not suitable for the baker's use. Each quarter of the above materials yields about 20 gallons of 58 per cent. spirit.

In Belgium and in some parts of North France the mash is prepared in sheet-iron fermentation or mash vats, provided with a stirring apparatus and a perforated false bottom. The mash vats are two-thirds filled with water at 80°. The grain worked consists of 33 parts of barley malt and 67 parts of ground rye. The proportions of grain and water are so arranged that there are 3 parts of water to 1 of groats and malt. After two hours' working, during which it becomes cooled, the wort is run off by means of a tap at the bottom of the mash vat, and cold water admitted in its place. The whole is united in the fermentation vat, and mixed with so much clear wash as will bring up the proportion of liquid to 7 or 8 parts to 1 of grain, a little more grain being used in the summer than in the winter. In the summer the fermentation is conducted at the lowest possible temperature, and about 9 lbs. of yeast are used to 500 gallons of liquor. In Belgium, on account of the local tax, the fermentation lasts only twenty-four hours. From 100 parts of material, about 25 or 26 parts of 95 per cent. spirit are obtained.

Manufacture of Spirit from Various Other Materials.—Besides the raw materials already described as being used in the production of alcohol, various others have been proposed, and some have been utilised.

Chestnuts and Acorns.—These amylaceous materials can undoubtedly be used in the spirit manufacture, where they can be collected in sufficient quantity and at a low price. They only require to be steamed and crushed, and their starch can then be converted into sugar by malt or sulphuric acid.

Asphodel.—The bulb of this liliaceous plant is very rich in sugar, and in the South of France and Algeria, where it grows wild abundantly, it can be used in the spirit manufacture. Its cultivation, however, could scarcely be recommended, as the bulb requires from three to five years to grow to any size. Alcohol has been obtained from the bulbs by rasping them, pressing out the juice, treating the residue with water and again pressing; then inducing fermentation in the liquor by the addition of yeast; 220 lbs. of bulbs yielded 14 pints of pure alcohol.

Jerusalem Artichoke.—The tubers of the Jerusalem artichoke (*Helianthus tuberosus*) contain, besides a large quantity of sugar, another body, inulin, closely allied to sugar and easily converted into it. The tubers are either rasped like beet roots, or steamed and crushed like potatoes, saccharised with a small quantity of malt, and then fermented like potato mash. The yield of alcohol amounts to 4½ per cent. of the weight of the tubers. The residue is good fodder for all kinds of cattle. As the cultivation of this plant is extraordinarily easy, it is worthy of more attention in the spirit manufacture than it receives at present.

Carrots contain a small quantity of sugar, and might be worked in a similar way to beet root, but probably not remuneratively.

Sugar Grass (*Sorghum saccharatum*).—At the time of ripening the sap throughout the entire plant is rich in sugar: it could be obtained by crushing and maceration. But as in temperate climates it is quite exceptional for this plant to ripen, it is of no importance to the spirit industry, although for several years it has been warmly recommended.

The Refuse Waters of the Spirit Manufacture.—The effluent water from the raw spirit factories where the residues are utilised, may be considered as harmless; the impurities from the washing of the potatoes are easily collected in settling pits; further, the water used in cleaning the fermenting vats and distillatory apparatus contains so little impurity, that it may be allowed to escape into the next watercourse. But the case is different with the water from the beet spirit factories, where the wash is not utilised or only partially so. Such water allowed to run into the streams or ditches would rapidly become putrescent, and produce all the evils, though in a higher degree, described under the sugar manufacture. Such impurities are best separated by filtration through the soil, but when land is not available the water may be disinfected according to Suvern's method, described before (p. 860).

When the spirit manufacture is combined with arrangements for the carbonisation of the residues, the gases issuing from the furnaces are no less offensive; they fill the air with repulsive smells, and give occasion to well-grounded complaints from the neighbours. The stinking substances, products of the dry distillation, and of the imperfect combustion of non-fermentescible constituents of the molasses, can be partially destroyed by maintaining behind the carbonising space a brightly burning fire, through which the gases pass before they escape into the air, But this only imperfectly accomplishes the object, since, it being necessary to obtain a good draught for

the oven, the gases necessarily pass too rapidly through the fire to be burnt to carbonic acid, water, and nitrogen. The difficulty is overcome in an imperfect way by carrying the vapour up through a tall chimney into a higher layer of the atmosphere, where it becomes diluted with so much pure air that its smell is less obvious.

Distillation of Wine Residues.—The residues left from the fermentation of wine, consisting of the skins, pulp, and stalks of the grapes, are saturated with wine, the alcohol in which can be recovered by distillation. For this purpose the simple apparatus shown in fig. 684 is used. The still (A) is surrounded by the fire space (B), and at a third of its height supports a perforated sheet-copper false bottom consisting

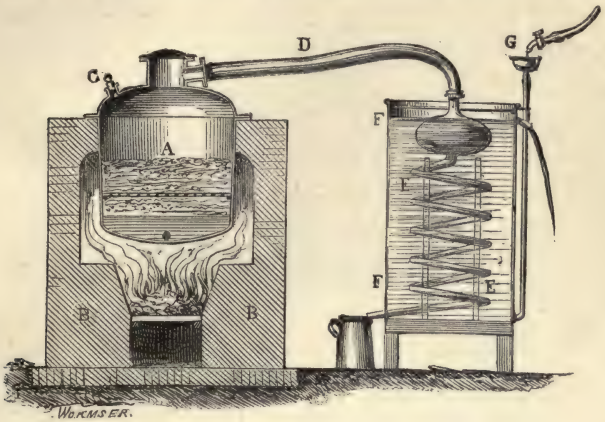


Fig. 684.

of two portions. The head of the still has a cover that can be hermetically closed, by the removal of which the lower part of the still up to the false bottom can be filled with water, the grape residues being placed on the false bottom. In the head of the still is a pipe (D) connecting it with the worm (E). The worm lies in the cooling vessel (F), which receives its supply of cold water at G. The fire (B) heats the water in the lower part of the still to boiling; the steam passes through the residues, converts the alcohol contained therein into vapour, and carries it forward into the worm. The heating is continued until only water passes over, the charring of the grape skins being prevented by the false bottom. When the distillation is ended the still is opened, the exhausted residue, which can be used for fodder, removed, and the still freshly charged. Of course such an apparatus could be much improved by a little modification.

PRODUCTION OF ALCOHOLIC BEVERAGES.

A variety of alcoholic liquors, prepared by fermenting the juice of grapes or other kinds of fruit, are in common use as beverages in most countries under the name of wine. Similar alcoholic liquids known under the name of beer, are prepared from infusions of malted grain and sometimes also from honey, molasses, and other saccharine materials. In Tartary another kind of alcoholic liquid known as koumiss is prepared from mare's milk.

Wine.—The art of making wine has been known from the remotest time of which there is any record. Among the early inhabitants of India, the use of wine by the Brahmins was prohibited, and only those not belonging to the caste were permitted to indulge in it. In Egypt also only the common people were allowed to drink wine, and the kings were required to abstain from it. The oldest records of the Israelites show that wine was known to them, but the priests were not allowed to drink wine upon the days when they had religious duties to perform. Wine was also known to the ancient Greeks, and it figures prominently even in their mythology. The Greeks further communicated a knowledge of the use of wine to the Romans, amongst whom women and children were by law prohibited from drinking wine, though, in spite of this restriction, the consumption of wine by all classes of Romans became very considerable at a later period. It was from the Romans that the Gauls and Germans learnt the art of making wine.

The original habitat of the vine is said to be the country on the shores of the Black Sea and Caspian Sea, where at the present time entire forests are overgrown by gigantic vines.

It is remarkable that, on the discovery of America, the vine was found to be flourishing there. More recently European varieties have been imported into that continent.

Constituents of Wine.—As regards composition, wine is to be regarded as more or less diluted alcohol, which also contains a number of other substances that communicate to it specific characters. Sweet wine contains sugar that has not undergone fermentation, and it is principally those kinds of wine that are made from highly saccharine must which contain sugar. In must of that nature, the whole of the sugar does not undergo conversion into alcohol, because fermentation is stopped as soon as a certain amount of alcohol has been formed. The sweetness of wine may sometimes be due to the presence of a large amount of glycerin. Sour wine contains a large amount of free acid, but the sour taste of wine is influenced by other circumstances besides the amount of free acids it contains. A wine containing comparatively little acid may taste more sour than another kind of wine containing more acid, provided it also contains a large amount of alcohol or glycerin, both of which mask the sour taste.

The strength of wine depends upon and is proportionate to the amount of alcohol it contains. Some wine contains, in addition to a large amount of alcohol, considerable proportions of the homologues of alcohol, viz., propyl alcohol, butyl alcohol, amyl alcohol, and the corresponding aldehydes. According to Maumené, the average composition of wine may be represented as follows:—

Water	from 89·1 to 90·0
Alcohol	„ 7·9 „ 8·0
Alcohol homologues, Ethers, Ethereal oil, Grape sugar, Glycerin	„ 3·0 „ 2·0

Some of these substances were contained in the must, but others, such as the alcohol and its homologues, as well as the ethers and aldehydes, glycerin, succinic acid, lactic acid, acetic acid, and carbonic acid, are products resulting from the fermentation. Lately an alkaloid has been detected in wine, as well as trimethylamine.

The proportion of solid residue left on evaporating wine to dryness at a steam heat varies very much according to the kind of wine; it may amount to only 1 per cent. or be as much as 20 per cent. Generally it ranges from 3 to 5 per cent., and it is only in the sweet wines which contain sugar that the extract amounts to more than 5 per cent.

The amount of alcohol in wine depends upon the proportion of sugar in the must before fermentation, and it varies considerably, as will be seen from the following table, which gives the average alcoholic contents of different kinds of wine:—

Port	from 18 to 20 per cent.
Madeira	„ 18 „ 19 „ „
Teneriffe	„ 16 „ 18½ „ „
Greek	„ 15 „ 18 „ „
Malaga	„ 12 „ 16 „ „
Lachryma Christi	„ 12 „ 15 „ „
Tokay	„ 10 „ 20 „ „
Lunel	„ 10 „ 13 „ „
Californian	„ 10 „ 14 „ „
Bordeaux	„ 9 „ 12 „ „
Burgundy	„ 9 „ 11 „ „
Hungarian	„ 9 „ 10 „ „

In Spain, Portugal, and France it is often customary to add some alcohol to wine, and in this case the whole of the alcohol in the wine of these countries does not originate from the sugar of the must.

The smell of wine, or, as it is termed, the bouquet, is due to a large number of substances that are present only in very minute proportions. At one time it was supposed that the odour of wine was due almost entirely to a substance called œnanthic ether, but it has since been ascertained that there are in wine several ethers besides that, as well as other compounds which contribute to the smell and modify it in different wines, viz., a great number of ethers of the fat acids, as ethylic acetate, ethylic propionate, ethylic butylate, caprylic, œnanthylic, capric, and caproic ethers; amyl and caprylic acetates, propylic butyrate, amylic valerianate, amylic malate,

ethylic tartrate, and amylic tartrate; also amylic, propylic, and butylic alcohols, with a small quantity of aldehyd and acetal, and probably some oleates, originating from the fatty oil of the gape kernels, contribute to the wine bouquet.

The formation of these ethers is due to the action of the wine acids on the alcohols, as shown in the following equation, taking, by way of example, the production of ethylic acetate by the action of acetic acid and alcohol:

$$\begin{matrix} C_2H_3O \\ H \end{matrix}\Big\}O + \begin{matrix} C_2H_5 \\ H \end{matrix}\Big\}O = \begin{matrix} C_2H_5 \\ C_2H_3O \end{matrix}\Big\}O + H_2O$$

The bouquet is produced partly during the fermentation and partly after, as well as during the storage. There is no fixed rule. Some wines acquire the chief bouquet after the completion of the fermen ation and lose it by longer storing, whilst other kinds of wine obtain the maximumt bouquet in the latter stage. The alcohol is produced by fermentation, and aldehyd is an intermediate product of the transition of alcohol into acetic acid, with possibly some acetal.

The acids and acid salts, if not present in too large a quantity, improve the taste of wine. These are chiefly tartaric acid and acid tartrate of potash (tartar), acetic acid, and in Italian wines also racemic acid, and in red wines, tannic acid. Citric acid and malic acid exist in wine in small quantities, together with succinic, and under some circumstances, lactic acid.

The total acidity, whether as free acids or as acid salts, varies between 0·2 and 0·8 per cent., calculating as free tartaric acid. Nevertheless, the taste of wine depends less upon the absolute quantity of acid present than upon the proportion the acid bears to the alcohol.

The amount of carbonic acid diminishes during the storing by diffusion through the pores of the casks, and becomes replaced by atmospheric air, of which the nitrogen only is dissolved, while the oxygen forms oxidation products.

New wine contains more than its own volume of carbonic acid, but this quantity decreases during the storage to one-fourth, and even less.

The colouring material of white wine existing only in small amount is but little known, but probably it is extracted partly from the grapes and partly from the wood of the casks.

The colouring matter of red wine, œnocyanin, is of a bluish-black colour, insoluble in water and in pure alcohol, but soluble in water containing a small quantity of tartaric acid. It is to be presumed therefore that the wine colour is dissolved by the alcohol and free acid, during the fermentation of the must with the husks. The colour is turned blue by alkalies, and is reddened by acids.

Böttger's test to distinguish the genuine red from the spurious colouring matter, which may be due to elderberries and alum water, or to mallow, bilberries, etc., is to dip a well-washed and white sponge into dilute hydrochloric acid, then into water, finally immersing it for some minutes in the suspected wine; the sponge is then washed with spring water, and if a spurious colouring matter has been employed, the sponge presents a bluish grey colour, whilst in the case of a natural wine it is hardly tinged.

In course of time the colouring matter of red wine forms with the tannic acid a compound which is precipitated on the sides of the bottles, thus gradually discolouring the wine.

Glycerin occurs in wine to the extent of 3 per cent., although generally under 1 per cent.; by long storage the quantity gradually decreases, so that hardly any is to be found in old wines.

The gum, or œnanthin, found in many kinds of wine, and supposed to be produced from sugar, gives the wine a thick consistency, but it is injurious if present in large quantity.

The ash of wine amounts to 0·2 or 0·3 per cent. by weight, and for the most part has the same composition as the ash of the must, with the exception that there are less carbonates, and that is accounted for by the separation during fermentation of tartar, which on ignition gives carbonate of potash. The constituents are chiefly potash and phosphoric acid; soda, lime, magnesia, ferric oxide, manganic oxide, carbonic acid, sulphuric acid and chlorine are also present.

The acid potassium tartrate that separates gradually in the crude tartar as the alcohol is formed, varies considerably in quantity. According to Fauré white Bordeaux contains between 0·1 and 0·15 per cent., and red Bordeaux between 0·06 and 0·2 per cent. The crude tartar also contains a small quantity of calcium tartrate.

The Grape and its Constituents.—A bunch of grapes consists of two parts, the stalk and the berry. The former consists chiefly of ligneous tissue, but contains among other substances a considerable amount of tannin, which passes into the must when the grapes are pressed with the stalks. In that case other constituents also

pass into the must besides tannin, such as acid salts, etc., and on this account, in making the finer kinds of wine, the stalks are separated from the grapes before these are pressed.

The grape consists of skin, juice, and kernel. The skin consists of a fine membrane formed of thick cellular tissue, and containing also some nitrogenous substances and silica. Immediately under the epidermis layer of the skin, there is a vascular tissue, which contains the colour substances, as well as tannin, nitrogenous substances, some ethereal oil and salts. The juice is hermetically enclosed in the skin, and is distributed between the cells and vessels. As regards composition it is to be considered as essentially a solution of grape sugar and fruit sugar in water. Besides these constituents it contains albuminous substances, pectin, colour substances, organic acids and salts; see p. 930. The juice amounts to about 94 or 97 per cent. of the total weight of the grape. The kernels contain cellulose, incrusting substance, fatty oil (about 12 per cent.), ethereal oil, tannin, nitrogenous substances, and ash.

There are upwards of a thousand different varieties of vines, corresponding to which there are as many different kinds of grapes. The most important are the following:—

1. Orleans; yellow berries which are highly saccharine. This variety is now less cultivated than formerly, as it yields a wine too poor in bouquet.

2. Riessling. The bunches are small and compact; the single berries are also small, and of a fine greenish-yellow colour, yielding a strong wine of a fine bouquet: this grape is used to produce the best Rhine and Moselle wine, *e.g.* Johannisberg, Rudesheim, and Brauneberg.

3. Traminer; small fleshy berries of red colour, yielding a very strong wine, such as those known in Germany by the names of Forster, Wachenheimer, St. Johann, etc.

4. Red Cleve or Rülander; the berries are red and ripen early.

5. Blue Cleve is grown in Burgundy and in the neighbourhood of Bordeaux, also in the Aar valley and on the Rhine.

6. Elbling; greenish-yellow berries, which do not yield a very strong wine. This kind of grape is very largely grown.

7. Gutedel comes from Spain; the berries are of a deep yellow colour, very translucent, and have very sweet juice.

The following kinds of grape are the most important as a source of wine: of the white kind of grapes, Sylvan or Austrian; Veltlin, Muscatel (Spain); Ortlieb (Alsace); of the blue or black kind, Sylvan (Austria); Tokay, Klöpf (Palatinate); Gänsfüss (Italy); Trolling (Italy); Malvoisie (Italy); and black Traminer, Elbling, Affenthal, Türkheim, etc.

Preparation of the Must.—The expressed juice of the grape is commonly known by this name, and it yields wine after having undergone fermentation. Its preparation involves two operations:—First, the gathering of the grape, and secondly, the expressing of the juice. The maximum quantity of sugar is found in the grapes which are the most ripe, and the ripening depends on the kind of grape, on the general climatic condition of the locality where it grows, as well as on the season. There are various kinds of grapes that ripen under equal climatic conditions at different times, and one and the same kind ripens earlier in warm and sunny places than in those which are less favoured. It is therefore impossible to have a definite period of the year for the grape gathering, and it is quite an irrational procedure to set apart a certain day in each year, as is customary in some parts of Austria, for the purpose of the grape gathering. In France it generally takes place in the first half of the month of October.

The grapes are cut very carefully with pruning knives or with shears, and in such a manner that not a single grape is spoilt by handling; then the bunches are placed in tubs and carried to the press-room. Here, if destined for making fine wine, they are sorted—the rotten and unripe grapes being separated for making poorer wine.

In many places the sorting is carried out during the process of gathering the grapes. The ripe grapes are first plucked, and the unripe grapes are left on the vines in order to ripen, and are then plucked in the same way. The grapes first gathered make the best wine. For the ordinary kinds of wine the grapes are pressed as gathered from the vines, but for fine wines it is necessary to separate the stalks before the pressing or treading operation to prevent the excessive contamination of the must with tannic acid. The grapes are generally separated from the stalks by hand labour, although machines have been constructed for the purpose. In the former method the grapes are plucked either by the hand or by a three-pronged fork, or rubbed over a wooden or iron grating, which only allows the grapes to pass. The machines are constructed to emulate the hand process, and consists either of a sieve on which the bunches of grapes are stirred round by an agitatory movement, so that the grapes fall through, or of forks by which the grapes are stripped off.

The squeezing or bruising of the grapes has the object of breaking up the skins so that the juice may flow out. It can be performed by hand labour or by machinery.

Where it is customary not to separate the stalks from the grapes, the crushing is performed in large wooden vats, either by the naked feet, or by wooden pestles. Sometimes the vats are provided with false bottoms perforated to allow the juice to flow through, so that it can be drawn off, or the crushing vats themselves have perforated bottoms through which the expressed juice can flow into receivers.

The grape-crusher has latterly been employed with advantage, instead of the feet and hand processes; it generally consists of two smooth wooden or iron rollers revolving in opposite directions, on which the grapes fall through a wooden cropper. The rollers, instead of being smooth, may be fluted.

Generally the bruised grapes are at once pressed, but sometimes the entire mass is allowed to stand for some days to acquire bouquet.

It is necessary to deviate from the usual procedure in order to prepare red wine. The blue or red grapes can be pressed at once after the gathering or bruising process; so can the white grapes when only a white wine is required, as the colouring matter is insoluble in water; but for red wine the grapes must stand in a loosely covered vat or tub for two to three days, or longer, up to three weeks and more, before being pressed. The alcohol meanwhile developed, together with the tartaric acid present, dissolve the colouring matter, which gives the red colour to the wine. At the same time, if the stalks have not been separated, a considerable quantity of tannic acid is dissolved from the skins and stalks. The wine thus acquires a harsh taste, but it keeps better, since the tannic acid also precipitates a part of the ferment.

As soon as the juice ferments, the skin and stalks are carried by the evolution of gas to the surface and form what is termed the head. Acetic acid is liable to be formed at this stage, and for this reason the long exposure to air in this state must be prevented as much as possible, either by frequently stirring up the mass, or by placing a grating on the surface, which will serve to keep down the head from the air.

The pressing is carried out by means of a lever press or screw press, employed either on the bruised grapes, or on the skins after the juice has drained out. The lever press is worked by means of a heavy wooden lever of about 30 to 50 feet in length, acting by its own weight, or loaded with a movable cradle filled with stones. The screw press is of a construction similar to a bookbinder's press. The pressing-plate has a raised edge to make the expressed must flow off at one point. Latterly, the press plates have been made of iron, having the advantage over wooden plates in not absorbing the juice, and in being more easily cleansed. The press of Orthlieb differs from the last described in having an iron cylinder instead of a flat plate, to contain the mass to be pressed.

Weniger's press consists of a cylindrical vessel made of oak laths bound by strong hoops. A wooden piston is set in motion by a crank working at the top, whilst a similar piston is worked from below. The expressed juice flowing through the laths is collected in a trough placed round the lath cylinders. This press has the advantage over the last one described that the grapes are pressed equally top and bottom, whilst by the one-sided pressure in the other case, and in consequence of the elasticity of the grape husks, the upper portion is more strongly pressed than the lower. Hydraulic presses have also been recommended, and there is no reason why they should not do good service where wine is extensively made, but it is necessary to guard against exerting too heavy a pressure, or other juices besides the true must will be expressed. Centrifugal machines have been latterly proposed instead of presses. Balard and Alcan obtained the following results from the same kind of grapes by the centrifugal process (with a previous pressure between two fluted rollers) and by simple pressing:

100 kilograms gave:—

	By the Centrifugal Process.	By Pressing.
Must	79·141 kilograms	77·068
Skins, etc.	20·214 „	18·601
Loss	0·645 „	4·331

A better yield is obtained by the centrifugal process, and it must also be taken into account that the necessary labour is a little less. This method has not at present found extensive use.

At different stages the must varies in quality. The first runnings obtained by bruising and by slight pressure from the ripest grapes is the sweetest. Stronger pressing yields a juice richer in the vegetable acids, and is therefore often separated from the first. By mixing the expressed skins with water, and then pressing the mass, a further quantity of must is obtained, forming by fermentation a thin wine.

The grape skins remaining after the extraction of the juice have been used for

various purposes. According to Petiot there is obtainable, by mixing them with sugar and water, then fermenting and pressing, a drinkable wine having a sufficient bouquet given to it by the skins and stones. The skins are also worked up for brandy, vinegar, and for potash; further they can be used as manure, for cattle provender, making verdigris, for gasmaking and for Frankfort black. Ilgen obtains by his process of dry distillation an illuminating gas, and a fine black residue of carbon.

Constituents of the Must.—The expressed grape juice consists essentially of an aqueous solution of grape sugar and fruit sugar. It contains also a great number of other substances which exist in relatively small quantity: for example, albuminoids, pectin, pectose, mucilage, organic acids, especially tartaric acid, together with some malic, tannic, and citric acids; a varying quantity of colouring material, fatty oils, and the ash constituents consisting of potash, soda, lime, magnesia, alumina, iron oxide, and manganese oxide. The bases are partly combined with the vegetable acids, and partly with chlorine, sulphuric acid, phosphoric acid, and silica.

Fresenius and Schliefer give the following analyses of must:—

	Klein-berger	White Austrian wine	Riessling	Red Ass-manhäuser	Johannis-berg
Grape and fruit sugar . .	10·590	13·780	15·14	17·28	19·24
Free acid	0·820	1·020	0·56	0·75	0·66
Albuminoids	0·622	0·832	—	—	—
Soluble pectin, mucous, and colouring matter . . .	—	—	3·46	—	2·95
Fatty substance and organic acids	0·220	0·498	—	—	—
Ash	0·377	0·360	—	—	—

The amount of sugar varies between 8 and 30 per cent. The ash has a very variable composition; it contains from 17 to 30 per cent. of potash, and in some cases as much as 70 per cent., 3 to 17 per cent. of phosphoric acid, a considerable quantity of lime (1 to 5 per cent.), ½ to 5 per cent. of magnesia, 1 to 5 per cent. sulphuric acid and carbonates. The sugar is estimated by the specific gravity method, which will be fully described in a succeeding section.

Fermentation of the Must.—This is caused by the same kind of ferment which serves to ferment beer wort, and the resulting products are much the same in character. The action of the ferment on the sugar of the must is to convert it into alcohol and carbonic acid, with the formation of some glycerin and succinic acid. A portion of the sugar is consumed in the production of the yeast cells.

The constituents to which the bouquet of wine is due, especially the ethers, are not direct products of the fermentation, but are formed partly during and partly after the fermentation.

The fermentation of wine appears to take place in three stages; the first or chief fermentation, the after fermentation, and the vat fermentation.

When the grapes are pressed, a sufficient number of the ferment germs to cause fermentation pass into the must, but their development depends on the must containing the nutriment, such as albuminoids, sugar, potash salts, and phosphates, necessary for the growth of the yeast fungus. The wine ferment is in every respect the same as beer yeast, which would ferment the must equally well.

Wine fermentation takes place in two ways, the superficial fermentation and the sedimentary fermentation, but the same care is not taken to ensure this as in beer fermentation. The first process occurs at a temperature of from 15° to 20°, and it serves chiefly for the production of the highly alcoholic wines of the south of France, Spain, Italy, Austria, and Hungary. These wines, however, have the disadvantage of being poor in bouquet; but by fermenting more slowly, and at a temperature of 5° to 15°, wine is produced, which, although poor in alcohol, is richer in bouquet. The sedimentary fermentation is practised chiefly in Germany, and especially in the Rhine provinces; but even in these places, at least to some extent, the must is subjected to the superficial fermentation, which very easily happens when the preliminary operations take place in hot weather, and the must has a proportionally high temperature.

The after fermentation is, under all circumstances, a very slow sedimentary fermentation, in consequence of the low temperature and the small amount of sugar remaining to be split up into alcohol and carbonic acid, with the formation of a little glycerin and succinic acid. The best temperature lies between 5° and 10°, but it must be low enough to extend the fermentation over a period of three months. In many places it is allowed to occupy five to six months. Besides the fermentation

proper, a series of other chemical changes occurs at this stage, and by the combination of acetic acid and its homologues, propionic and œnanthic acids, or lactic and succinic acids, with ethylic and amylic alcohol, the ethers which give the bouquet to the wine are formed.

Experiments which have been made recently tend to show that after the fermentation is quite over the wine hardly contains any sugar, and that the sweet taste of the wine is due to glycerin (amounting to 3 per cent.)

The ethers and the bouquet increase during the store fermentation, but as sugar is now absent no fermentation proper takes place; the wine becomes stronger, that is, richer in alcohol, which arises from water being diffused through the pores of the wooden vat and evaporating from its surface whilst the alcohol is unaffected.

It is a common opinion that in spring wine undergoes a renewed fermentation. This is erroneous. The escape of wine from the bung-holes of the cask in spring time is more probably due to the expansion of the wine in the casks. The gases which have been absorbed in great quantity by the cold wine in winter also escape as the temperature rises, and it is this fact which has given rise to the supposition that a further fermentation takes place.

In stored wine there is a gradual loss of carbonic acid, but not to such an extent as might be expected when it is considered that, even in a well-bunged vat, there is a continual diffusion of the carbonic acid and the external air through the pores of the cask. Wine can be stored up for ten years without losing more than one half to a third of its carbonic acid. This is due to the solubility of carbonic acid in alcohol and in alcoholic liquids.

It is still a doubtful question whether air should have access to wine during fermentation. It is certain that the chief fermentation proceeds more quickly if air has been driven through the must at the commencement. Various kinds of apparatus have been constructed for the purpose of aerating the must. In some cases, a centrifugal machine is used, or air is forced in by a bellows provided with a rose nozzle. Wine so aerated will keep better, because the oxygen of the air oxidises and precipitates the nitrogenous compounds which are easily decomposed in this way. It is very important, however, in this manner of operating to keep the temperature very low, otherwise a considerable quantity of the bouquet will be carried away. As the ethereal oils are only formed and retained when the action of the atmospheric oxygen is exerted it is necessary to determine by experiment whether the bouquet is being increased or lessened by the continued action of the air.

It has been also proposed to let the after fermentation proceed at a low temperature in open vessels, somewhat similarly to the plan carried out during the fermentation of beer wort. The wine, thus made, keeps better, but there is generally a loss of bouquet, in consequence of the separation of nitrogenous substances.

During the vat fermentation there is a slow oxidation of certain nitrogenous compounds, which, if not thus destroyed, would spoil the wine by favouring the formation of acetic acid. Air gains access to the wine through the pores of the vat. But the quantity of air entering in this way being small, it is recommended in some cases to stop the bung-hole of the vat with wadding in order that there may be more free access of air. If this plan be adopted the vat is varnished, so that air can only enter through the wadding which serves to filter the spores and germs, because by so much exposure to air there is much scope for acetous formation.

For the first fermentation of must capacious vats either of wood, sandstone, or brick set in cement, are generally used. Latterly glass has been proposed, but it has had no general application. A suitable cover serves to prevent the admission of a superabundance of air, whilst a hole in the cover, or a small tube, serves as an exit for the carbonic acid gas. In some places, in order to prevent the admission of air, a valve is fitted to the apparatus, and can only be opened from within by the pressure of the carbonic acid gas. The fermentation tube of Kölges and Bamberger effects the same purpose; it consists of a glass tube bent twice at right angles, having one end through the bung-hole, with the other or exit end reaching into water. The carbonic acid gas bubbles through the water, and the admission of air is thus prevented. If the top of the vat be fastened down, or is very large, it is provided with a hole for the purpose of running in the must with or without the skins and emptying out the residue. A thermometer also passes through the top into the wine. At the lower part of the vat a cock is placed for the purpose of drawing off the wine. In Germany, instead of using large vats, it is the custom to employ many large casks, either having an open bung-hole, or an arrangement as above described. In the fermentation of red wine, which is always carried out without separating the grape skins, an open vat is used, provided with a perforated inner shelf, and this is placed some inches below the level of the liquid in order to prevent the rising up of the husks.

After the must has been a short time in the fermenting vat it shows signs of

working; the temperature rises, a foam forms on the surface, and there is a disengagement of carbonic acid. The skins are carried to the surface, and, if for too long a time exposed to the air, an acid fermentation results; and it is to prevent this surface exposure of the husks that the above-mentioned perforated shelf is fitted below the level of the liquid. In the first few days the temperature rises until it is about 5° above the temperature of the air, and at the same time the disengagement of carbonic acid increases, but after the first fermentation the evolution diminishes to such a degree that there is no further perceptible disengagement of gas. The time occupied in the first part of the fermentation depends upon the temperature of the fermenting room. In Germany it varies from 8 to 14 days, in France for the ordinary kinds of wine from 3 to 8 days, in the department of Herault from 12 to 14 days, and in some places, where the finer sorts of wine are prepared, the fermentation proceeds during 4 to 6 weeks.

In proportion as the must ceases to ferment, and in consequence of the conversion of sugar into alcohol, the specific gravity of the liquid diminishes, this furnishing a very ready means of ascertaining the progress of the fermentation. Since alcohol as well as the ethereal and bouquet-giving compounds would be carried away by a very brisk first fermentation, it is advisable to cool the must by means of cooling tubes or by ice, so as to moderate the fermentation.

Various contrivances have been proposed to collect the alcohol escaping with the carbonic acid gas, and a very simple one consists in making the gas pass through water by means of what is termed an hydraulic bung. The quantity of alcohol escaping may be as much as ½ per cent. of the total quantity present in the wine.

The carbonic acid gas evolved can be used for the preparation of bicarbonate of soda, white lead, etc., but it is not generally utilised.

After the chief fermentation is over the wine is run into large casks, care being taken that the yeast and lees remain behind; the casks are filled to the bung to prevent as much as possible acetic acid forming by the atmospheric action.

During the after fermentation the yeast is deposited at the bottom of the casks, the sides of which are also gradually coated with a crust of tartar which is insoluble in the alcohol now present in the wine.

The crude tartar, which is from time to time removed from the empty casks, consists chiefly of acid tartrate or potash, generally with some admixture of calcium carbonate and calcium tartrate, ferric oxide, colouring matter, yeast residues, etc.

When the after fermentation is finished the casks are either filled up and closed or the wine is at once run into the storing casks, where it is bunged up until a considerable further deposition of tartar has taken place, and then it is racked off either into casks or bottles. This racking process must be repeated from time to time with wine that is being stored for a very long time.

Before filling the casks with wine, they must be thoroughly cleansed from any mildew which would tend to cause the production of acetic acid; for the destruction of such fungi the casks are steamed and fumigated with sulphur.

Fining or clarifying is carried out only with wine which is not clear after fermentation. It serves to get rid of the suspended matter, which if allowed to remain would cause an after fermentation in the hot seasons of spring and summer. In the case of red wine, which contains tannin, the fining is effected with albumin or gelatin in the form of blood or solution of glue, which form insoluble compounds with the tannin, and in this way the suspended matter in the wine is precipitated.

White wine, which contains no tannin or but very little, has the required quantity of tannin added in the form of oak bark or gall nuts, and it is then clarified with isinglass, as in beer fining. The precautions necessary in fining wine are that the wine is not disturbed and that the finings are not in separate pieces but in a coherent net-like mass.

Milk, acting by the coagulation of the casein, has also been used for wine fining, as well as wood shavings, which act by virtue of the tannic acid they contain, and even paper pulp, gypsum, alumina, alum, etc., have been recommended for the same purpose, but isinglass or albumin is usually preferred. Fining powders generally contain one or more of the above-mentioned substances.

In order to effect the improvement of inferior wines, either of two purposes or both may have to be served, viz., to increase the amount of alcohol and to decrease the acidity. Sometimes also bouquet is given to the wine by artificial means. Either the must or the wine is operated on according to the object desired.

One of the oldest methods is that known as the Chaptal process, according to which, if there be more than 0·6 per cent. of acid in the must, enough carbonate of lime is added to reduce the acid to that amount. To increase the amount of alcohol raw sugar is added. The Gall process is intended to be applied to the wine produced in bad seasons by adding sufficient water to reduce the amount of acid to 0·5 or 0·6 per cent. and then mixing with diluted must enough grape sugar to make the total

quantity about 20 per cent. The fermentation is then carried out in the ordinary way. The process is to be recommended when the must is poor in sugar but rich in acid, and it is quite capable of producing drinkable wine.

The grape sugar employed in the Gall process is prepared by the action of dilute sulphuric acid on starch. It is commonly known under the name of starch sugar, and differs from pure grape sugar by containing in addition a considerable quantity of dextrin.

Neutral potassium tartrate, calcium carbonate, or sugar lime may also be used to neutralise the excess of free acid.

The amount of alcohol may be increased by freezing the wine and removing the frozen portion with the adhering albumin and tartar; or by the direct addition of alcohol obtained by the distillation of wine or by adding pure spirit. Gypsum, through its affinity for water, will effect this object to some extent.

In Scheele's process, the sour taste is masked and the sweetness increased by adding from 1 to 3 per cent. of pure distilled glycerin. The glycerin preserves the wine, and there is no fear of the sweetness of the wine diminishing, whilst wine sweetened with sugar is liable to fermentation, which may alter its character.

An extract of grape blossom is frequently used to improve the bouquet of wine.

Some years ago experiments were made in France with the view of applying electricity to the preservation and improvement of wine. It had been observed that some wine which had run out of casks destroyed by lightning had a very fine flavour.

The method of obtaining wine from the grape skins, according to Petiot, depends upon the fact that the skins after pressing still contain so considerable a quantity of bouquet-forming substances that, by digesting them with a solution of sugar, an artificial must is obtained, which, by fermentation, acquires the odour and taste of good wine. The constituents which it may be deficient in, such as tannin, tartar, etc., can be subsequently added.

At present Petiot's method is only carried out with the residuary skins from the preparation of red wine. The wine produced in this way is strong, rich in bouquet, retains its properties, is of a fine colour, and not unfrequently it is of a better taste than that produced from the first must, which in bad years easily becomes sour.

By good management the deterioration of wine can be prevented, and, if it takes place, artificial means may be employed to remedy the defects.

Wine becomes sour by acetous fermentation, or by the formation of lactic acid, especially when it contains a considerable amount of albuminous substances and little alcohol. The best means of prevention is to keep the wine as much as possible from contact with atmospheric oxygen by filling the casks to the bung, or by soundly bunging them up when the after fermentation is completed. In the event of mildew appearing, the wine must be quickly racked off into fresh casks; the introduction of carbonic acid has the effect of killing the *Mycoderma aceti*, and the neutralisation of the acid with concentrated potash solution will sometimes produce drinkable wine.

Mould is sometimes formed upon the surface of wine when the casks are not full, and the cellars are too warm, and the bungs are not closed. This defect can be counteracted by sulphuring, either by burning some sulphur in the empty part of the cask, or by racking off the wine into a fresh cask in which sulphur has been previously burnt. Solution of sulphurous acid may be used for the same purpose.

The bitterness in wine, more prevalent in old than in new wines, is likewise due to a peculiar ferment which produces a bitter principle of an unknown chemical constitution, and although present in small quantities it gives a very bitter taste to the wine. It is stated that isinglass or carbonate of lime will sometimes remove the bitterness.

Sweetness, due to the presence of unconverted sugar, occurs when, in consequence of a late vintage, the temperature of the air is too low to admit of complete fermentation, which will then frequently proceed so slowly that after months or even years the wine remains sweet.

Wine is rendered thick or turbid by a peculiar ferment which decomposes the tartaric acid of the tartar with evolution of carbonic acid, and also decomposes any sugar and glycerin that may be present. The ferment floating about the wine causes a disturbed and thick appearance, and ultimately the wine becomes sour. The evil can be obviated by decanting the wine when the contact with air causes the fermenting agent to be precipitated. Red wine chiefly suffers from this defect. Viscidity or ropiness is due to mucous fermentation, by which sugar is converted into mannite and mucilage. It has been stated that the ferment by which this change is produced originates from vegetable gelatin left in solution during the fermentation and storing, owing to insufficient contact with atmospheric oxygen. The evil may sometimes be remedied by adding tannin in the form of a decoction of the grape stalks and kernels. Exposure to air is less efficacious.

The taste of the cask is due to the use of dirty casks and is very difficult to be got rid of. The best plan is to rack the wine off quickly into a new cask, and to mix with it about ½ per cent. by volume of olive oil, which helps to remove the unpleasant taste.

Red wine sometimes presents a bluish or brown discoloration, when the tartar has been converted by putrid fermentation into carbonate of potash. The original colour is restored by careful addition of tartaric acid sufficient to reproduce the tartar.

Preservation of Wine.—Weak wines do not bear exportation so well as strong wines; it is the custom therefore to mix with them two to three per cent of alcohol.

Although wine generally keeps better in bottles than in the casks, there is the disadvantage that the cork may give a taste to the wine. This especially occurs when the cellar is damp and mildew accumulates on the cork; to prevent this the corks are covered with rosin or with tin capsules.

Freezing is one of the means by which wine may be preserved. This treatment facilitates the precipitation of the dissolved or suspended nitrogenous substances which give rise to the formation of ferments, and at the same time, when the frozen portion is removed, the wine is rendered stronger or more alcoholic since only the water is frozen.

Another method of greater importance consists, according to Oppert, in heating the wine contained in bottles or in hermetically sealed vessels in a water bath at 70°; this process is said to give a wine which afterwards retains its properties for many years. Beaune wine treated in this way remained good after it had been two years at sea. The preservative effect of this treatment is no doubt due to the destruction of ferment vegetation.

Several forms of apparatus have been devised for treating wine by this method.

The arrangement adopted by Rossignol is represented by fig. 685. It consists of a cask having the bottom replaced by the copper pan (c) which is tinned on the outside and ends in an open tube (*c*). The wine to be treated is run into the cask, and the copper vessel is filled with water which is heated by the furnace underneath. Care must be taken to keep the water below the boiling point, and to maintain it at a temperature just higher than that to which the wine requires to be heated.

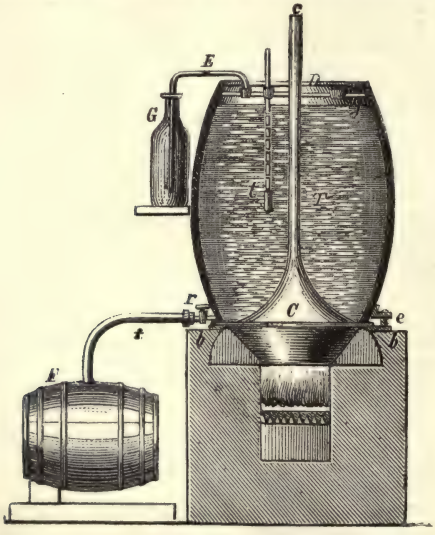


Fig. 685.

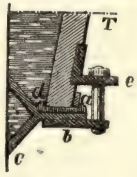


Fig. 686.

When the proper temperature of 50° to 60°, as shown by the thermometer (*t*), has been reached, the wine is drawn off into the cask (F) by the cock (*r*) and the india-rubber pipe (*f*). The cask (T) is refilled with wine, and the same operation carried out as before. At intervals water is run in to cleanse the cask, otherwise the wine dregs deposited during the operation would decompose on the admission of air, and would impart an unpleasant taste to the wine subsequently heated.

In fig. 686 is shown the connection at the bottom of the apparatus between the wine cask and water vessel. (*a*) is a tinned copper ring soldered to the water reservoir

(c) fig. 685, and between the ring and the edge of the cask lies the india-rubber ring (*d*), against which *a* is so strongly pressed by screw bolts fixed on one side in a strong iron ring (*b*), and on the other in a piece of angle iron (*e*) fastened to one of the iron hoops of the cask, that a perfect joint is made.

As it is necessary to keep the wine from contact with air on account of its action on the colour and taste of the wine, and as the cask must be quite filled with wine, a pipe (E) made of glass or tin conducts the overflow due to expansion into the bottle (G).

The wine is drawn off into casks whilst hot, and as it cools an air space results through contraction which must be quickly filled up with hot wine. Instead of this method the casks used for racking the hot wine are connected with each other by a bent pipe, so that the wine passes from one to another as the contents cool.

Wine which has been put into casks in this manner can be transported without risk of deterioration, in addition to which the wine can be stored in casks for a longer time without being racked off, and there is no need for cool store cellars.

Results obtained by this method are very favourable, inasmuch as it turns out a wine which will retain its properties, and has no tendency to the ordinary wine maladies; the method is extensively used in France.

Adulteration of Wines.—Wine may be considered adulterated when mixed with substances injurious to health, either for the purpose of imitating a wine of a finer sort, or to raise its value. In this class must be included those wines which have had a substance added to counteract some objectionable character, such as too great acidity.

Large quantities of wine are met with which are merely imitations of the better kinds of wine, and they are prepared partly from inferior wine by the addition of artificial ethers, extracts, and essences; sometimes also without any basis of real wine. For the detection of such falsifications there is a want of any decisive test beyond the indications afforded by the taste or smell.

Wine that has become sour is sometimes treated with acetate of lead, in order to remove the acidity, and in such cases the wine is liable to contain lead, which can be readily detected by means of sulphuretted hydrogen.

Copper or zinc, derived from the copper or brass vat fittings, can be detected in a similar manner.

Sulphate of iron, which is sometimes added to wine, may be detected by the blue colour which is produced upon the addition of potassium ferrocyanide.

The colour of wine is produced artificially in many instances. Light red or white wines are coloured by the addition of some innocuous red colouring matter.

In France the colouring of red wines by means of fuchsine, or aniline red, is said to have been extensively practised within the last few years; and since this material is liable to contain arsenic, its use for such a purpose would be highly objectionable. Much attention has recently been paid to this subject in France with a view to detect the admixture of this colouring matter.

The distinguishing features of the genuine colouring matters have already been given, and the following reactions with acetate of lead, and alum and carbonate of ammonia, may serve for the detection of the common spurious materials which are used:—

	With Acetate of Lead	With Alum and Carbonate of Ammonia.
Pure red wine	bluish grey	dirty green
Poppies	dirty grey	slate grey
Elder berries	dirty green	bluish grey
Bilberries	greyish green	bright violet
Privet berries	green	,, green
Dwarf elder berries	bluish grey to violet in the fresh berries, and fine green in the fermented extract	bright violet
Mallow flowers	dark green	bluish violet
Logwood	feeble dark blue	dark violet
Brazil wood	wine red	carmine red

In the event of the colouring matter having been added after or before fermentation, the adulteration may be detected by the microscope; for, if a drop of uncoloured wine be examined under the microscope, it appears when dry quite homogeneous, whilst in case of the addition of colouring matter after fermentation separate clots of colour can be seen.

White wine is coloured with burnt sugar. Dark wines can be decolourized by agitation with animal charcoal.

The testing of Must and Wine.—Must is chiefly tested for its amount of sugar, and less frequently for the amount of acid.

The amount of sugar is determined by a special form of hydrometer, the degrees of which show the amount of sugar.

In estimating the percentage of sugar in must by the specific gravity, it is assumed that it is only the sugar which affects the specific gravity. It must, however, be borne in mind that the dissolved protein compounds, organic acids, and the ash constituents all tend to raise the specific gravity.

The following table gives the specific gravity corrected for the soluble compounds other than sugar:

Corrected sp. gr.	Per cent. of sugar.	Corrected sp. gr.	Per cent. of sugar.
1·010	3	1·0657	17
1·016	4	1·0744	18
1·020	5	1·0788	19
1·024	6	1·0832	20
1·028	7	1·0877	21
1·032	8	1·0922	22
1·036	9	1·0967	23
1·040	10	1·1013	24
1·042	11	1·1059	25
1·044	12	1·1106	26
1·048	13	1·1153	27
1·053	14	1·1200	28
1·0572	15	1·1247	29
1·0614	16	1·1295	30

The amount of acid in must is determined volumetrically by means of a solution of lime of such a strength that 27·5 cubic cent. equal 0·06125 grm. sulphuric acid; 0·075 grm. acetic acid; 0·09375 grm. tartaric acid; and 0·235 grm. acid tartrate of potash.

Ten c.c. of the clear must are brought into a beaker without litmus, and the lime water is added from a burette until by the change in the colour the neutral point is obtained. The reading of the burette is taken, and the percentage of acid can be calculated.

When the must is not clear, lime water is added, insufficient to saturate the acid; the liquor is then filtered, and more lime water is added to the filtrate until alteration of colour takes place.

Wine is chiefly tested to ascertain the amount of alcohol, and seldom for the acidity or the amount of extract.

Direct determination of specific gravity is of no value, because it is influenced by other constituents besides the alcohol.

Guy-Lussac's apparatus, or a modification of it, is used for the purpose of ascertaining the alcoholic contents of a wine. A measured volume being taken, it is distilled into a graduated receiver, and the distillate made up to the original quantity. In the distillate the alcohol is estimated by an alcoholometer.

Silbermann proposes a method which is much quicker than that just described. It depends upon the expansion of alcohol between 0° and 78° being three times as great as that of water.

Conaty's ebullioscope indicates the amount of alcohol in a mixture of alcohol and water, by the temperature of the vapour given off from the boiling liquid.

The vaporimeter of Geissler is based upon the fact that the tension of alcohol vapour is much greater than that of water vapour. The alcoholic liquid is heated in an enclosed vessel, in connection with a kind of manometer, in the outer arm of which the mercury rises to an extent proportionate to the amount of alcohol, which is indicated upon a scale.

The volatile ethers and the homologous alcohols affect the result. In using this method carbonic acid must first be removed by shaking with caustic lime.

The acidity of wine is ascertained by titration. Instead of litmus as an indicator Mohr recommends an alcoholic tincture of logwood, and to add the normal soda solution until the yellow colour of the logwood changes to violet.

The amount of extract is determined by evaporating a known quantity of wine to dryness on a platinum disk on the water bath, and weighing the residue dried at 100° to 110°.

Treatment of the Wine Residues.—The grape skins, after the expression of the juice, are frequently distilled to make brandy. With this object the skins are subjected to fermentation, and then distilled.

Crude tartar can be obtained from the residue of distillation. For this purpose the skins are separated by a sieve from the hot liquor, which is allowed to stand for some time until the tartar is deposited. The residue on the sieve can be either

incinerated to obtain potash, or merely carbonised for vine-black. It has also been used for making gas.

In some places the skins are used as cattle fodder or as manure, and for preparing verdigris. By allowing them to undergo acetic fermentation, and filling them alternately with sheet copper in a warm place, a coating of neutral cupric acetate is thus formed, which is gradually converted into basic acetate, or verdigris.

Tannic acid, and a fat oil which can be extracted by carbon bisulphide, are to be obtained from the grape stones.

The wine lees are distilled for brandy; the last product which passes over consists of wine oil, which is essentially œnanthic ether. The residue of the distillation can be used for preparing crude tartar or potash.

The crude tartar deposited in the after fermentation is purified, and also used in the preparation of tartaric acid.

Beer.—Beer was known to the Egyptians, and it is probable that the Greeks learnt from them the art of brewing. The Romans obtained their knowledge of beer from the Gauls, and like them, called it cerevisia. In Germany the brewing of beer has been carried on during many centuries, it being mentioned by Tacitus. As long as the malt required was prepared in each house, the beer industry remained comparatively undeveloped, but when the monasteries began to brew on a larger scale it attained a considerable perfection. The monks were the first to make a distinction between single beer and double beer, the former being called convent, the latter pater beer. The use of hops in brewing dates from the ninth century. White beer was first brewed in Nüremberg in 1541. The brewing of ale and porter dates only from the eighteenth century.

Beer contains, besides the alcohol produced by fermentation, some dextrin, small quantities of nitrogenous substances, some of the ash constituents of the malt, and dissolved carbonic acid, which contributes essentially to its good quality. When beer is kept, carbonic acid is given off continually to a small extent; so that, to keep the liquor saturated with this gas, a constant reproduction of it within the beer itself is necessary. Beer is a beverage drunk while in a state of fermentation, thus differing essentially from wine and like beverages, which are only fit for use when the fermentation is over. As soon therefore as beer, through standing in partly filled vessels, in too warm a place, or any other cause, ceases to evolve as much carbonic acid as is given off, it loses its freshness; the same thing happens when fermentation is stopped either by too low a temperature or complete decomposition of the sugar.

Beer left to stand exposed to the air easily turns sour, especially when it contains much ferment, as is the case with superficially fermented beer, acetic acid being formed from the alcohol. Beer that has once turned sour, cannot be reconverted into good beer, and the best use that can be made of it is to treat it for vinegar.

In order to preserve beer, especially for export, a number of plans have been proposed. One of the best of these is that recommended by Velten. It consists in heating the beer during twenty minutes or an hour in closed vessels to a temperature of 48° or 50°. To secure quick heating, so that the temperature does not remain long between 25°–40°, when too strong fermentation would ensue, the vessels are heated in a water bath. The most suitable vessels for the purpose are made of metal, and furnished with a stirring apparatus made of pipes, through which steam is passed. The beer is then filled into casks and charged with carbonic acid gas. In using the above method, it is necessary that the escape of carbonic acid during the heating process should be entirely prevented.

According to the relative proportions of the several constituents—alcohol, aromatic substances, and the non-volatile constituents which are collectively designated malt extract—beer has different characters. Beer with body, as ale and porter, the Brunswick Mum, etc., contains from 8–15 per cent. malt extract, while thin beer contains only from 4–6 per cent. of extract. The amount of alcohol in beer also varies, though dry or thin kinds of beer sometimes contain more alcohol than beer with body. The strong English beer contains 5 and even 8 per cent. of alcohol, Bavarian beer from 2 to 5 per cent. and the more ordinary kinds from 2 to 3 per cent. The relative quantity of carbonic acid in beer varies between 0·1 and 0·2 per cent.; the sugar from 0·2 to 1·9 per cent., the dextrin from 3 to 5 per cent. and upwards, the albuminous substances from $\frac{1}{4}$ to $\frac{3}{4}$ per cent. Besides carbonic acid, acetic, lactic, and some succinic acids are contained in beer. According to A. Vogel's researches the proportion of lactic acid to acetic acid in fresh beer is tolerably constant, as 32 to 1; in beer exposed to the air the proportion of acetic acid increases rapidly. Tannic acid is not always present in beer, and then only in very small quantity. The amount of ash yielded by beer varies between 0·1 and 0·3 per cent. According to Martino, who analysed Erlanger beer, it consists essentially of potash (37 per cent.), soda (8 per cent.), magnesia (5$\frac{1}{2}$ per cent.), phosphoric acid (32 per cent.), silicic acid (11 per cent.), and

naturally varies according to the raw material used in brewing. According to Lermer, beer contains an organic base the nature of which is at present unknown. Besides the constituents mentioned, beer also contains the entire constituents of the hop, as well as glycerin and caramel.

The following table shows the results of Lermer's analysis of different kinds of Munich beer. 100 parts were found to contain:

	Alcohol	Extract	Albumen	Ash	Phosphoric acid in 100 parts of ash
Bock beer from the Court brewery	5·08	7·83	0·87	0·28	34·18
Summer beer „ „ „	3·88	4·93	0·43	0·23	32·05
White beer „ „ „	3·51	4·73	0·53	0·15	26·57
Spaten Bock beer	5·23	8·50	—	—	—
Zacherl Salvator beer	4·49	9·63	0·67	—	—
Löwenbräu winter beer	3·00	5·92	—	0·25	29·28

The following table shows the percentage of alcohol and extract in English, German, and other kinds of beer:—

	Alcohol	Extractive matter
Porter (Barclay and Perkins)	5·4	6·0
London porter	6·9	6·8
Burton ale	5·9	14·0–19·3
Scotch ale	8·5	10·9
Bavarian jung beer	3·3–4	5–6
„ lager beer	4·4–5·1	4–5
Munich schenk beer	3·8–4	5·4–6·3
„ lager beer	4·3–5·1	5
Würzburg lager beer	4·0–4·7	4·4
Munich bock beer	4·3–4·8	8·6–9·4
„ salvator beer	4 6	9·0–9·4
Prague lager beer	4·8	10
Nüremberg lager beer	3·8–4·0	4–6
Bamberg schenk beer	4·2	5–9
„ lager beer	4·2	4–6
Brussels lager beer	5·5	3·4
Culnbach lager beer	4·2	4–6
Erlanger lager beer	3·8	4–6
Brunswick mum	2·4	39·0–45

The residue left in the mash tuns and known under the name of brewers' grains is used as fodder for cattle. The germs separated from the malt by sifting as well as the exhausted hops form a good manure. Brewer's yeast is extensively employed in bread making, and in spirit manufacture.

The different kinds of beer are prepared by fermenting infusions of malted grain —generally barley—so as to convert the sugar they contain into alcohol.

Raw Materials of Brewing.—The principal material used in brewing is barley; and though wheat, oats, maize, potatoes, rice, and starch, are capable of undergoing the necessary changes for the development of sugar, they are scarcely ever used.

The barley used for brewing is the product of a species of *Hordeum*. It requires to be ripe and sound; this may be in part ascertained from its external appearance. Each grain should have a uniform light yellow colour extending to the tips; it should be full, plump, quite white and mealy inside, and free from odour; and there should be no admixture of foreign or dead grains. Especially the barley should be heavy, as when malted it yields the saccharine principle nearly in proportion to its weight. Scotch barley weighs from 54 to 59 lbs. per bushel; English barley 52 to 58 lbs.; and Saale (German) barley 50 to 54 lbs. In order to promote its uniform germination, the barley used in a malting operation should, as far as possible, have been grown under similar conditions and on the same soil. This may be tested by placing some of the grains in a shallow dish, covering them $\frac{1}{8}$ to $\frac{1}{4}$ of an inch with water, and then exposing them without drying to a temperature of 25°–30°. When the barley is good, the grains will germinate simultaneously.

In the individual grains, the mealy interior alone is of value in beer brewing; the husk, owing to its containing easily decomposable substances, which would give the beer an unpleasant taste and smell, should be removed as far as possible.

The principal constituents of the internal mealy portion of the grain, which is built up of concentric rings increasing in thickness towards the outside, are starch and gluten; besides which there are small quantities of albumin, a fatty oil, and inorganic matter. As starch is the constituent most important in beer brewing, its properties in this respect may be briefly enumerated. When heated with water, starch forms a paste which, in contact with decomposing nitrogenous substances, is easily converted into lactic acid; with tannic acid, however, it forms a compound insoluble in water, that readily sinks to the bottom. When starch is roasted, dextrin, a substance soluble in water, is formed, which constitutes a chief constituent of beer; other empyreumatic substances are also produced, upon which the flavour of the beer essentially depends. The diastase, formed from the gluten during malting, changes the starch—most favourably at a temperature of from 60°–75°—into dextrin and sugar, and these in their turn by fermentation yield alcohol and carbonic acid.

In this country and in France sugar has also been used as a brewing material, raw sugar, molasses, or grape sugar being available for this purpose. Such an addition is generally economically advantageous, since a part of the grain is saved and the work facilitated. Further, beer thus prepared keeps better, because less barley being used there is introduced into it a smaller quantity of the nitrogenous compounds which render it more liable to spoil. But this beer, rich in sugar, is less pleasant to the taste than that containing more dextrin, on which account it appears to be preferable to add an amylaceous substance to the grain, and potato starch is often employed. Still, the oily constituent of potatoes may easily impart an unpleasant taste to the beer; Zehling therefore recommends that the potatoes should be treated with soda previous to use.

Hops.—The peculiar aromatic taste of beer is in great part due to hops, the unfructified female flowers of the hop plant (*Humulus lupulus*). The strobiles of this plant—the hops of the brewer—contain between the bracts at the base a peculiar granular sticky substance, known as yellow powder, hop meal, or lupulin, which, together with the scales, contain the essential constituents of the hop for the purpose of brewing. Wild hops produce these constituents in only very small quantities, therefore cultivated hops can alone be used by the brewer.

According to Wimmer (I and II), and Raubert (III), there is contained in 100 parts:—

	I Scales	II Yellow powder	III Ellinger Stadt hops
Oil of hop	0	0·12	0·50
Resin	2·60	2·91	15·90
Peculiar bitter substance	4·68	3·01	not determined
Tannic acid	1·61	0·63	3·02
Gum	5·83	1·26	11·10
Cellulose	63·95	8·99	48·33
Extract solution in water	12·12	4·92	6·40

The aromatic taste and smell of beer is chiefly due to the oil of hop, while the bitter resin contained in the strobiles, which, owing to its solubility in alcohol, passes into the beer, often imparts to it an unpleasant bitter taste. The peculiar bitter substance mentioned in the above analysis is soluble in water, and consequently also passes into the beer, imparting to it a part of its bitter quality, but at the same time rendering it more permanent and wholesome.

The tannic acid contained in hops is so far of importance that a quicker clarification of the wort is dependent upon it, as it forms, with the mucilaginous substances in the wort, insoluble compounds which readily settle to the bottom.

The relative proportion of the active constituents in the hops varies considerably, depending upon culture, the season, soil, and other circumstances. Certain districts are especially celebrated for the hops produced by them; such are Kent and Nottingham in this country, Saatz and Pilsen in Bohemia, Nüremberg and Spalt in Bavaria, Schwetzingen and Mannheim in Baden, in Brunswick, Thuringia, and other districts.

The quality of a sample of hops may be to some extent judged from external appearances. The strobiles should be clean and of good size, not mixed with leaves or stalks, and should be either light red or greenish yellow in colour. Very ripe hops

are blood red, while those which are unripe are quite green. The sample should be rich in yellow powder, and this should be sulphur yellow, not brown, as is the case in old hops; when rubbed between the fingers it should leave a resinous sticky mark, and at the same time evolve a strong pure hop odour. Seeding hops are not so good. Hops should not be more than one year old, since they quickly lose their active properties, and may impart to the beer an unpleasant taste and smell from the hop oil having turned rancid. Old hops may be detected by the seeds falling out when the strobiles are broken, while the seeds of fresh hops remain fast.

The proper carrying out of the hop harvest is a matter of great importance to the quality of the beer to be produced. It is essential to choose for it dry weather, and a selection should be made of the ripe hops, the unripe being left to ripen.

Great care is also required in drying the hops; they must be dried quickly and thoroughly. The drying is carried out either in large airy garrets or in special drying apparatus of which the Hohenheim hop kiln presents the most advantages. It consists of a large inclined drying surface, formed of hurdles covered with warm sackcloth, the hurdles being laid over shallow boxes through which warm air is driven by means of a ventilator. The air passes through the hurdles upon which the hops are laid and rapidly effects their drying. The hops are turned by placing an empty hurdle upon a full one, and turning both over in such a way that the fresh one comes to be the bottom one, the other is then removed.

Hops also require careful storing. The plan of storing up hops in lofts is objectionable, since the exposure to air and moisture rapidly changes them. In order to exclude air as completely as possible, the thoroughly dried hops should be packed tightly together. A very common way of packing hops consists in placing them in sacks and pressing them down with the feet; this is, however, insufficient. In this country, as well as in America, hydraulic presses are used for pressing hops, the resinous nature of the hops then causes them to stick well together, and hops thus pressed will keep for two or three years without deterioration. Hops are said to keep still better when the sacks in which they are pressed are papered externally.

The bad appearance of old hops may often be diminished by sulphuring. Sulphurous acid, however, admits of ready detection. By Wagner's method a small quantity of the hops to be tested is placed in a glass flask with a small quantity of zinc and dilute hydrochloric acid, and the gas evolved is conducted into a very weak solution of sodium nitroprusside. If the hops have been treated with sulphurous acid, sulphuretted hydrogen is given off, which produces a beautiful violet coloration in the solution of sodium nitroprusside. The presence of sulphurous acid does not, however, always indicate old hops, because frequently in this country fresh hops are sulphured in order to preserve them.

Brainard's method of preserving hops consists in storing them up in chambers at an average temperature varying as little as possible from 10°, and not exposed to light and air.

With this object the thoroughly dry hops are packed in dry sacks and stored in chambers situated on the north side of a building, built of waterproof materials, and which can be well closed. The hop-chamber is furnished with a double wall all round, the space between the two walls communicating with an ice-house, so as to keep the temperature of the interior as low as possible. Hops thus stored in such chambers are said to keep for years without altering.

Schaar's method is somewhat similar to the above, consisting in burying the hops in pitched tubs in ice.

Instead of using the hops themselves in beer brewing, it has been suggested to boil the hops in suitable distilling vessels, so as to separate the essential oil as a distillate, which together with the thick extract left behind is preserved for subsequent addition to the beer.

But, setting aside the fact that in the preparation of this extract changes take place in the essential constituents which impart to the product an entirely different taste and smell, the method cannot be recommended owing to the facility it affords for adulteration.

Water.—It is by no means a matter of indifference what kind of water is used in beer brewing, inasmuch as each admixture contained in natural water has an effect upon the quality of the beer.

Rain water is fit only for softening the grain, because it is contaminated with organic germs floating in the air, which easily produce decomposition. Filtered rain water freed from such germs is on the other hand well adapted for beer brewing.

Of the different kinds of well and spring water the softest, *i.e.*, that which contains relatively the least calcium salts in solution, is the most suitable for the brewer. A hard water may be to some extent softened by exposing it for some time in large reservoirs to the action of the air. Water thus prepared may be used for brewing.

River water, which as a soft water would generally be adapted for brewing purposes, has the disadvantage of being turbid from the presence of suspended organic and inorganic or earthy matter. This may, however, be removed by filtration through gravel, sand, or charcoal.

According to Siemens a water adapted to brewing purposes must have the following properties: it should be pure and clear, it should possess neither smell nor harsh flavour, it should not be rendered cloudy by solution of soap, nor should it yield any perceptible deposit when boiled; legumes, such as peas and lentils, when boiled in it, ought very speedily to soften, and it should not evolve any odour when kept for some time in a warm place.

Yeast.—Yeast also belongs to those substances indispensable in brewing, and has been already considered under FERMENTATION (see p. 881).

Malting.—The conversion of grain into malt has for its object the formation of diastase, which originates in the gluten during the malting. Partly during the malting and partly in the following mashing process, this diastase effects the conversion of the starch contained in the grain into grape sugar and dextrin. There are also produced during the drying of malt in kilns some dextrin, together with caramel and empyreumatic substances, which communicate to beer its colour, and have some influence on the flavour and aroma.

The process of malting comprises the following operations:—(1) Steeping or softening the grain. (2) Germination. (3) Drying. (4) Removing the germs. (5) Bruising the malt.

The steeping or softening of the grain has for its object to impregnate the grain with sufficient water to cause germination, and also to remove from the husks extractive substances which would spoil the taste of the beer. The barley is placed in large cisterns of wood, or preferably of stone or cast iron, with four times its volume of water, and kept in the cisterns until the points of the grains upon being pressed with the hand allow of the ready separation of husk and contents. Such grains as after two or three hours, during which time the mixture is frequently stirred, remain floating on the surface, are taken off and separated. The most suitable temperature for the steeping is 15°; and the water is usually changed every twelve or twenty-four hours, in summer more frequently than in winter. The time during which the grain requires to be steeped varies; old barley containing much gluten requires from four to six days, while young grain does not require more than thirty-six or thirty-eight hours. In winter the process proceeds more slowly than in summer. Too long steeping deprives the grain of its germinating power.

When the operation is completed the water is let off as quickly as possible by means of cocks with a large bore, so as to prevent one part of the grain from remaining immersed much longer than the rest. The water drawn off has a yellow colour due to the substances dissolved.

Wheat, on account of its weaker husk, requires less time for steeping than barley. Barley loses during steeping from 1 to 2 per cent. of dry substance; but by the absorption of water its weight is increased about 47 per cent.

Germination.—The object of germination is the formation of diastase from the gluten of the grain during the development of the cotyledon, in order to make use of this diastase afterwards for changing the starch into sugar and dextrin. The proper germination of the grain is therefore one of the most important operations in beer brewing. Diastase must be formed in quantity sufficient to change the entire quantity of starch, otherwise starch would be lost. The germination should not however be allowed to proceed too far, since then starch would again be lost by being used up by the young plant in the formation of cellular tissue. The germination must be stopped as soon as the germs have attained a length of $1\frac{1}{3}$–$1\frac{2}{3}$ of the length of the grains, or when the cotyledon has penetrated about half way into the interior of the grain.

The chamber in which the germination is carried out should be as independent as possible of fluctuations of temperature and changes of weather, the most suitable temperature being 10° to 15°. Although a moist chamber is required for due growth it should not be musty, since that is apt to cause fungoid growth. Constant change of air is necessary. If the chamber should be insufficiently humid a spray of water or a jet of steam may be introduced. In Germany a cellar is usually employed 5 to $6\frac{1}{2}$ feet high, and called the germinating floor. The floor of the malting room should be hard and impenetrable to moisture; it is generally made of good cement or stone flags lying close together, the bedding beneath depending upon the situation. On a damp soil building rubbish is used, and clay in dry places. The sides and ceiling of the chamber are covered with hydraulic cement. It is essential to avoid having any ruts or holes, into which grains can fall, because they quickly rot, and mould is formed

by which the sound grain in subsequent operations may be easily injured. Spring is better suited for malting than summer or winter, the temperature in March or April being more constant, and the germination taking place more uniformly. Beer brewed in March owes its good quality partly to this fact. Autumn is equally favourable for the operations of malting.

The treatment of the germinating grain upon the malting floor varies. In this country and in North Germany the swollen barley, after the water has drained off, is made up into heaps, 4 to 6 inches high, and when these have got dry on the surface they are turned over in order to secure an equal temperature of 10°–15° and equal moisture throughout the whole heap. Directly the grains exhibit a whitish projection they are made up into heaps, 12 to 14 inches high. The vital activity of the grains causes a rise of temperature in the heaps, and when it has risen to 25°–27° the so-called sweating takes place, the hand becoming moistened when thrust into the mass. The heaps are now so turned that the upper and lower layers come more into the centre, the middle layer being brought to the surface and next the floor, so as to reduce its temperature. Should the grain not be sufficiently moist, or if it has been too suddenly dried, it is then carefully moistened with lukewarm water.

In turning over the heaps the grain gets more and more spread out. When the plumules are sufficiently developed the malting heap is spread out in a heap, 4 inches deep, so as to avoid further heating of the grains, and allow the further development of the germs to go on slowly. The germination is considered complete when the germs in the case of barley have attained the length of $1\frac{1}{2}$–$1\frac{2}{3}$ of the original grain.

In Bavaria the following plan is universally adopted. The softened barley is spread out upon the malting floor in level heaps, 5 to 6 inches high, and turned as often as the surface becomes dry, which takes place about two or three times daily. The turning is effected with a flat shovel in such a way that the lower layer is brought to the surface and *vice versâ*. The grains begin to germinate in two or three days and then the heap is made higher, about 10 to 12 inches, and left until the temperature of the interior has attained at most 25° or 27°, and a strong sweating appears on the surface. The heap is then again turned, divided into three parts so that the middle or warmed part of it is brought next the floor, upon it what was the uppermost portion, and finally upon that which was lowest. In the course of about ten hours a further sweating takes place, and a further turning of the heap is necessary. After three turnings the germs generally attain the desired length of half an inch, and the grain is again spread out. The heap is thus reduced 3 to 4 inches in depth and the operation repeated as often as is necessary to avoid any further important rise of temperature. The process is generally complete after three spreadings.

During the warm part of the year the germination lasts on an average ten or twelve days, at the end of the autumn fourteen days to three weeks are necessary.

To prevent further growth of the germs, the grain is removed to the drying floor, or, as the case may be, to the charring floor. The drying floor is a spacious airy room, upon the floor of which the grain is spread out in thin layers, and turned from time to time.

The loss of dry substance in malting is about 3 per cent. A considerable quantity of carbonic acid is given off during the operation; well-ventilated chambers are therefore necessary to prevent danger to the workmen.

The change which takes place in the composition of grain during malting may be seen from Saussure's analysis of germinated and ungerminated barley.

	Ungerminated	Germinated
Starch	72·7	65·8
Cellulose	5·5	5·6
Sugar	2·4	5·1
Dextrin	3·5	7·9
Gluten and mucin	11·8	7·6
Albumin	1·4	2·7

The subsequent operations depend upon whether the germinated grain is to be treated for air-dried or roasted malt. The brewer uses almost exclusively roasted malt, but some kinds of beer of fine quality are prepared from air-dried malt alone.

Malt roasting.—The object of roasting malt is not only to dry it, but also to produce empyreumatic substances which influence the colour and taste of the beer brewed from it.

The roasting must be so conducted that the malt is uniformly heated, but at the beginning, while the grain is yet moist, not too strongly, so as to avoid formation of

paste, which upon drying would leave a horny mass impervious to water. As soon however as the malt is dry, the temperature is raised to 90° or even 100°, since at this temperature diastase no longer acts upon the starch except in the presence of water, nor is it itself decomposed.

The kilns used for roasting malt are known as smoke kilns, air kilns, and steam kilns.

A smoke kiln of old construction, but which is in use at the present day, consists of a horizontal perforated metal plate or wirewove frame of copper or iron wire, 16 to 20 feet long, the holes or interstices in which must be small enough to prevent the grain slipping through. The roasting plate is supported by cross beams and iron pillars, the whole being mounted upon brickwork narrowing towards its lower end. The hot air from the fire passes through the apertures in the plate into the lower part of the kiln, where it mixes with cold air admitted from outside, the rate of transmission of which can be regulated so as to lower or raise the temperature as may be required.

The most suitable fuel for these kilns is that which yields as little smoke as possible; dry coal, or what is still better, the best quality of coke is the most convenient fuel. If wood, brown coal, or turf be used, the malt would acquire a darker colour and a smoky taste which afterwards passes into the beer.

In air kilns the roasting plate is heated by hot air, which is admitted below or produced in the lower part of the roasting chamber by heating tubes through which hot air from a furnace is made to pass.

The Overbeck kiln, with a new combination of roasting plate, is represented by fig. 687. Each of the three stories (A B C) consists of three endless cloths running upon a pair of rollers. The malt is carried along upon the cloths in an upward direction; the cloths themselves are made of material specially constructed for the purpose, and are furnished at the sides with edges bent at right angles, to prevent the malt falling out. The texture of the cloths is such as to enable them to bear the continual bending and stretching to which they are subjected without injury. Between the roasting cloths of the two upper stories are turning arrangements, by which the malt falling from the highest parts of the wire cloths is thrown about 3 feet high against a peculiarly bent metal cover, which then conducts it to the beginning of the cloth next following in succession. At the end of the floors where at *a* and *b* the malt falls from a height of 9 feet upon the hurdle beneath, as well as between the cloths of the lower stories, turning arrangements have been found to be superfluous. The way in which this turning apparatus works is of great utility in brewing, since not only is the mixture of green malt and germs completely separated, but the malt is mixed at regular intervals, the individual grains being projected through the air, forming upon falling layers of malt of the same evenness and equality of depth as they passed from the feeding hopper (E). The most practised hands are not able to turn the malt with anything like the regularity effected by this apparatus. By means of special simple contrivances, consisting in bringing rims along the edges of the chambers, the roasting chambers are so thoroughly closed that hot air from the furnace (*o*) is compelled to pass over the malt. As a rule, the malt takes about two and a half hours to pass over the first roaster, completing the second one in about three and a quarter hours, and the lowest in about four hours. This different ratio of time admits of an almost equal spreading of malt in all three stories, since the volume of malt diminishes in drying in about an inverse ratio. The roasting process is generally complete in about ten hours; it admits however of being lengthened or shortened by altering the driving belts. After passing the last chamber, the malt finally falls upon a travelling bed (*p*), which removes it from the

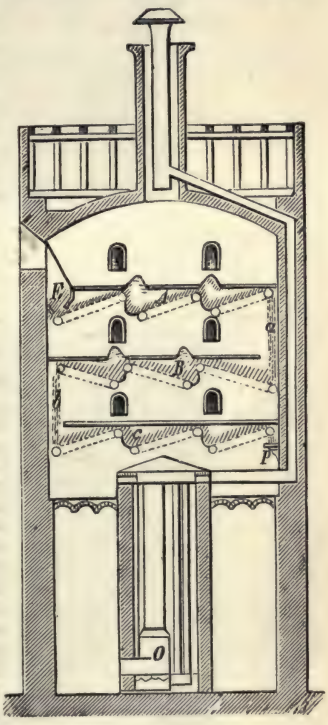


FIG. 687.

kiln. The kiln admits of being worked by one man, and gives excellent results both quantitative and qualitative.

Figs. 688 and 689 represent an air kiln of Siemens' construction, in which the heating is effected either by waste hot air from the boilers, or by means of special heating arrange-

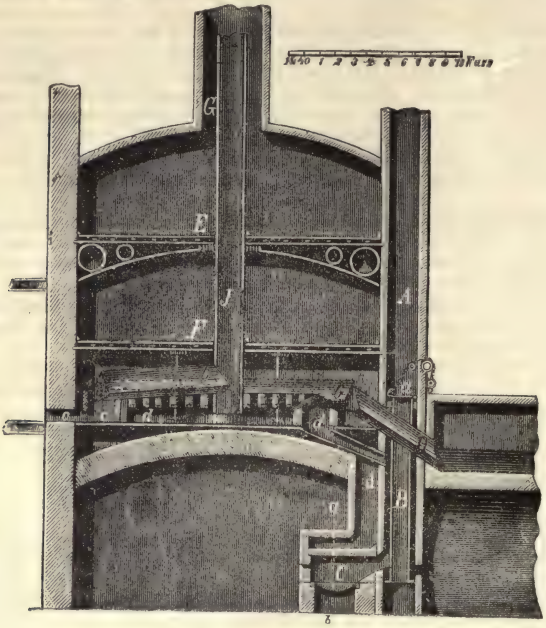


Fig. 688.

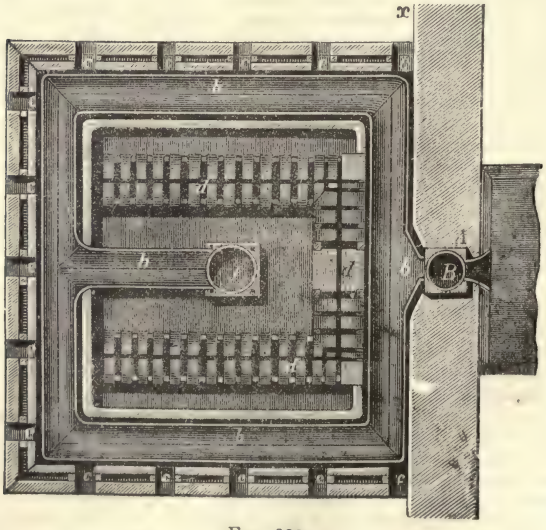


Fig. 689.

ment. A couple of roasting plates are placed one above the other, an alteration which has recently been much introduced in the air kilns. The upper plate is for drying,

the lower one for the actual roasting process. A is a common chimney for hot air from the boilers and kiln fire, *x* a fire-proof wall, B an iron cylinder into which passes the hot air of a special oven (C), or the hot air escaping from the boilers is conducted by means of the flue (D) which is furnished with a valve (*a*) for turning the hot air into the cylinder (B) or the chimney (A). At a distance of 4 or 5 inches the cylinder B is surrounded by a casing of fire brick closed above, and communicating with the lower part of the roasting chamber by a number of flues. A hollow space formed by the casing of the oven (C) communicates with this series of flues; cold air from outside passes through the side apertures (*c c*), beneath the heating tubes (*b b*), and from thence beneath the roasting plate. The heating or smoke tubes (*b b*) extend from the cylinder (B) through the roasting chamber, and join again in the chimney (*J*), which conducts the gases into the air through the steam pipe (G), and at the same time by its heat promotes the quick evaporation of moisture from the kiln. There is also another series of flues (*d d*) through which air heated at the outside of the cylinder (B) by the oven (C) is at once conducted to the roasting plate. The hot air rises from it through slits which increase in width with their distance from the cylinder B and the furnace C, so as to obtain as great an equality as possible. F and E are the two roasting plates.

In the steam kilns the air conducted beneath the roasting plate is heated by making superheated steam circulate in iron or copper tubes in the lowest part of the roasting chamber. This kind of kiln is only fit for preparing a pale kind of malt, and is little employed.

The malt is spread out on the several roasting plates in layers about 3 to 5 inches deep, a little shallower in the case of double roasting plates than where simple roasting plates are used, since otherwise the draught would be insufficient. For the reason already given, the temperature before the water has been got rid of requires to be very moderate; it ought not to exceed 60°. Subsequently the temperature is raised to 90° and 100°, in Bavaria indeed to 120° and still higher. The temperature is regulated according to the degree of roasting desired: for pale malt and that used in distilleries the roasting temperature is not allowed to exceed 60°.

As already mentioned, beer is also prepared from air-dried malt. As a rule the colour of beer depends upon the duration of the roasting, and the temperature at which it is carried out; the longer the roasting process, and the higher the temperature, the greater is the proportion of dextrin formed and the darker is the beer. It is now very usual to impart to beer a dark brown colour by adding strongly roasted malt or sugar to the wort prepared from pale malt.

Working with a kiln with a simple roasting plate, the proportion of malt daily roasted is reckoned for every 100 square feet roasting surface as follows: once emptying, about 4 cwts.; twice emptying, about 6 cwts.; three times emptying, 8 to 10 cwts.

The removal of the shoots or cornings must follow directly after the roasting, since they absorb moisture upon keeping, lose their brittleness, and become afterwards hard to remove. The removal is necessary, because they contain no constituents essential to beer, and they would increase the volume of the malt without improving it, and would furthermore render the beer liable to turn sour.

The methods of removing the cornings are very various. An old plan which is still much in use consists in treading the roasted malt with the feet and then passing it through sieves. This method, however, involves the loss of a good deal of malt. A newer method consists in passing the freshly roasted malt through a sieve drum, to the axis of which arms furnished with brushes are attached, and finally through a winnowing machine. In the former the cornings are broken off by the motion of the drum and the brushes, and in the second they are separated from the malt grains. Drums, with pieces of metal attached to the sides, by means of which the grains are raised and thrown down upon the axle of the drum, are also in use for effecting separation.

The cornings amount to about 3 per cent. of the entire weight of the malt, and they are used either for fodder or manure. Including this 3 per cent. the total loss during malting amounts to about 8 or 10 per cent. of the dry substance of the grain employed. Besides this, the loss of moisture amounts to about 10 or 12 per cent.

According to the recent researches of John, the loss of dry substance in malting is still more considerable, 100 parts of dry barley yielding—

Malt (excluding plumules and radicles) . . .	83·09	85·88
Plumules	3·56	3·09
Radicles	4·99	4·65
Evolved as gas	8·36	6·38
	100·00	100·00

Bruising.—Malt contains about two-thirds of its weight of soluble substances. In order to facilitate the solution of these substances, it is first of all necessary to break the malt grains, a process known as malt bruising. In this operation the malt grains are rather crushed than ground, the husks being thus removed, but not ground up. The malt, before being submitted to the bruising process, is moistened either by exposing it to the air and allowing it to absorb moisture naturally, or it is sprinkled over with from 7 to 10 per cent. of water. Millstones or iron rollers are used in malt bruising, care being taken that they are not set too near one another, but so far apart as to crush without pulverising the malt.

The bruising mills consist of a couple of smooth cast-iron rollers of different diameter revolving in opposite directions, the malt being passed to them by means of a sloping perforated plate of sheet iron, through which dust and fragments of cornings fall into suitable receptacles. At the extremity of the plate, where the malt falls over, revolves a wooden roller, the periphery of which is furnished lengthwise with knife blades just long enough to touch the iron plates. A slow motion being given to this drum, the knife blades push forward just enough malt to feed the mill, so that the latter can never get over-filled. The whole is surrounded by a wooden casing, narrowed beneath the rollers to the shape of a funnel, through which the bruised malt falls either into some vessel for collecting it or direct into the mash tub.

The moistening causes an increase of 16 per cent. in the volume of the malt, and the bruising a further increase of 16–18 per cent.

The composition of malt is shown by the following analyses by Oudemanns:

	Pale roasted malt	Strongly roasted malt
Starch	58·6	47·6
Sugar	0·7	0·9
Dextrin	6·6	10·2
Caramel	7·3	14·0
Cellulose	10·8	11·5
Albumin	10·4	10·5
Fat	2·4	2·6
Ash	2·7	2·7

In this country malt is generally prepared in buildings especially erected for that purpose situated in grain districts, the owners of such malt kilns selling the malt to the brewer; but in Germany and France malting is carried on for the most part in the breweries. Recently the English system has been partly adopted in Germany.

In this place may be mentioned Fleck's process of preparing malt without germination, which consists essentially in treating barley with dilute (1 per cent.) mineral acids, those most adapted for the purpose being sulphuric acid and nitric acid. In this process care must be taken to avoid the use of more liquid than is absolutely necessary, as what is called glass malt is apt to be produced in the subsequent operation of roasting. For complete softening 100 parts of barley would require 80 parts of acidulated water, but complete softening is not allowed. The conversion of starch into sugar by means of acidulated water is accelerated by gentle heating. After heating 50 parts of barley and 30 parts of acidulated water, containing 1 per cent. of sulphuric acid, for seventy-two hours over a water bath at a temperature of 40°, the conversion of the starch is so far complete that after drying and roasting good malt is obtained.

A disadvantage attending this process consists in the loss of phosphoric acid, it being replaced by the mineral acid and passing into solution. On the other hand, the loss of starch (sugar) and of organic substances in general is considerably less than in the germinating process, since the change effected by mineral acids is not accompanied by the formation of shoots.

Brewing.—In making beer from malt, the first consideration is the conversion of the starch still contained in the malt into dextrin and sugar, then the fermentation of this sugar, and its conversion into alcohol and carbonic acid. Beer brewing comprises the following operations:—1. Mashing and solution of soluble extractive constituents. 2. Boiling and hopping of the wort. 3. Cooling of the wort. 4. Fermentation of the wort.

1. **Mashing.**—The object of mashing is to convert the starch still contained in the bruised malt into dextrin and sugar by the action of the diastase. This conversion is effected by stirring up the malt with warm water, in which the diastase dissolves and then acts upon the starch. The temperature at which the mashing is

conducted is of great influence upon the rapidity of the mashing process. Schwarzer's researches have proved that diastase, when heated above 65°, is gradually decomposed, and is then no longer capable of converting starch into sugar and dextrin. Hence when it is desired to mash with as little malt (diastase) as possible a temperature of 60° or 65° must not be exceeded. When, however, a quick conversion of starch into sugar is desired, the mashing temperature is allowed to come as high as 75°, although at this temperature a considerable loss of diastase ensues, and consequently more malt is required. The mashing temperature is further of considerable influence upon the proportion of sugar and dextrin produced. At all temperatures from 60° down to 0°, whatever the quantity of diastase used, there is always produced from 50 to 53 per cent. of sugar from the starch extract. At higher temperatures proportionally less sugar and dextrin is formed.

It is a matter of importance in mashing that the water should come into intimate contact with the starch of the bruised malt, both to dissolve the sugar formed and to secure the complete action of the diastase.

According to the way in which the mashing is effected two distinct operations may be distinguished—the infusion method, and the decoction method.

The mash tuns are large round or square tubs with double bottoms, generally made of oak, sometimes of iron or stone. The upper bottoms set a few inches above the lower ones are perforated, and they are generally made of wood, although copper or iron is preferable, since metallic bottoms allow of finer perforations than wooden ones, thus rendering a more complete separation of the malt residue from the wort possible. Between the two bottoms is a tap for running off the liquor passing through the perforated bottom. A tube let in below feeds the tub with hot water. A more recent construction does away with false bottoms, instead of which strips of metal grating are let in with channels beneath them for conducting away the liquor.

The stirring of the mash in the mash tun was formerly always effected with an iron rake. At the present time, it is more frequently effected by machinery, especially in large breweries.

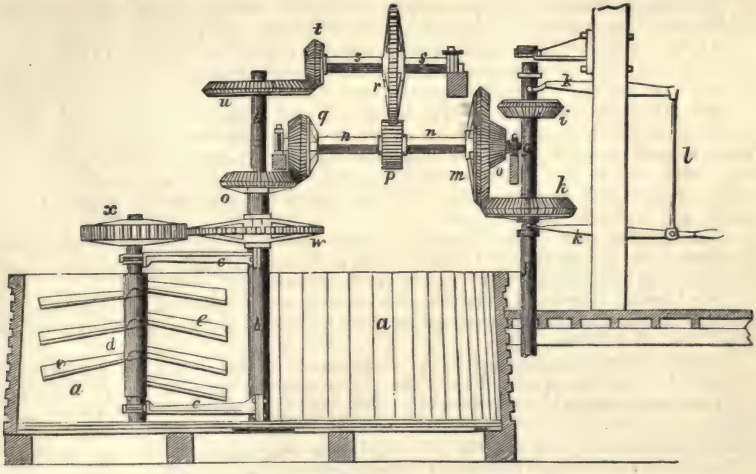


Fig. 690.

Fig. 690 represents a mash tun with stirring apparatus. The tun itself (*a a*) is made of wooden staves hooped together. In the centre is fixed a perpendicular shaft (*b b*), which can be revolved slowly by the bevelled wheels (*t u*) at the top. From one side of this shaft project two arms (*c c*), attached to the spur-wheel (*w*), and carrying at the other extremity a shaft (*d*) which is furnished with a number of arms (*e e*) placed obliquely and made to revolve by the wheel (*x*), so that when the shaft is turned, these arms stir the malt in the tun and constantly lift it upwards from the bottom.

Another form of mash tun is represented by fig. 691. The stirrers (A and B) are turned by the pulley (*p*), the pinion (*b*), and the driving-wheels (C F F′ and G). Outside the lower part of the side of the wooden vat (I I) is a casing, allow-

ing sufficient free space for heating the mash in it by opening the steam cock (o), the steam passing to the pans through the valve (*m*) or escaping through the cock (*r*). In most cases, however, this arrangement for warming the mash tun is omitted.

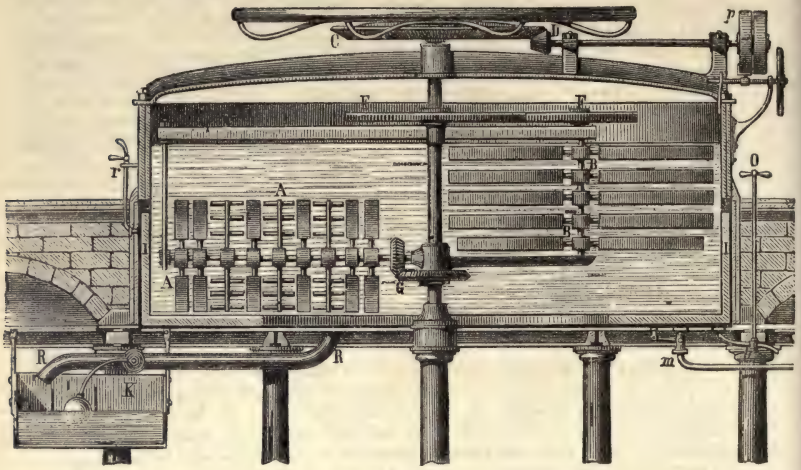


Fig. 691.

Above the mash tun is often fitted a movable lid by which it may be partly or entirely covered.

Beneath the mash tun is a reservoir (K) called the underback, for the reception of the wort escaping from the tun through the discharge pipe (R R).

An apparatus for quickly wetting the bruised malt has been devised by Steel, and has been adopted in a number of breweries. It consists of a horizontal iron cylinder $2\frac{1}{2}$ feet long and $1\frac{1}{2}$ to 1 foot in diameter, one end of which is completely closed with an iron plate, the other extremity partly so. A spiral shaft furnished with knives passes along the interior of the cylinder, and is set in motion when the cylinder is in use. Bruised malt and water are thrown in together through a wide tube towards the closed end of the cylinder, and having been well worked up together by the stirrer, fall out into the mash tun at the other end of the cylinder, the upper half of which only is closed.

The brewing vats serve either for heating water and wort, or for boiling and hopping, or the two operations are carried out in separate vessels. In the latter case the mash tun is made somewhat larger than the brewing vat.

The brewing vessels are round with flat bottoms, and are generally made of copper, although recently iron has been used in their construction. The hot air circulates round and below them.

A matter of great importance in the production of a good wort is the temperature at which the mashing is carried on. The proper mashing temperature, *i.e.* the temperature most favourable for the action of diastase upon starch, is between 65° and 75°; it is not advisable however to start with this temperature, but the mash should be gradually heated to it, the rise of temperature being made slower when working with slightly roasted malt than when strongly roasted malt is operated upon.

Infusion method.—This method, which is adopted in this country and in France, and to some extent in Germany, is as follows:—Directly the malt is placed upon the perforated bottom of the mash tun a quantity of water at a temperature of 60°, equal to about one and a half times the weight of the malt, is passed into the mash tun from below, the whole being well stirred by some suitable arrangement, and then allowed to stand about half an hour, so as to secure the penetration of the water. A fresh quantity of water at a temperature of 90° is then run in, so as to raise the whole to 70°–75°. After again well stirring, the mash tun is covered and left quiet for about three hours, during which time the diastase acts upon the starch, forming sugar and dextrin. Upon opening a cock, the liquid or wort passes through the perforated bottom of the mash tun into the wort reservoir or underback, from whence it is pumped into the copper, or in some cases, as above mentioned, it is pumped at once into the copper.

The first extraction withdraws from malt about three-fifths of its soluble constituents, but a portion still remains with water in the malt grains: 100 lbs. of malt retaining from 100–120 lbs. of water. In order therefore to extract the malt, as well as to render soluble the still undissolved farinaceous constituents, the residue is treated with about half the quantity of water employed in the first instance at a temperature of 80°, again mashed, and after standing an hour, during which time the last portion of starch is converted into sugar, the wort is run off and mixed with the results of the first mashing.

The boiling method.—This method is especially adopted in Bavaria and neighbouring parts. The bruised malt is first of all made into a paste, in the mash tun, with a small quantity of cold water. After four to six hours, another portion of water is heated in the copper to boiling, and gradually run into the mash tun until the liquid has attained a temperature of 30°–36°. After a short time the thicker portion of the liquid is brought into the brewing vat, where it is boiled under constant stirring for half an hour or an hour, and then again run into the mash tun, raising the temperature to 55°. After protracted mashing, another portion of the mash is brought into the vat, again boiled, and this second thick mash is returned, by which the temperature of the contents of the mash tun are raised to 70°. The clear mash is then run off through the perforated bottom of the mash tun, brought into the boiling vat, where it is boiled for a quarter of an hour, and then again run into the mash tun, the temperature of the latter being thus raised to 75°. After protracted stirring the mash tun is covered, and its contents are left quiet for one to one and a half hours; the wort is then run off through the perforated bottom.

Augsburg method.—The essential difference between this and the foregoing method consists in the liquor yielded in the first mashing with cold water being run off through the perforated bottom into the under back. This liquor, called kalter satz, contains a considerable quantity of dissolved albumen. A portion of it is mixed with the water to be heated in the copper, and boiled for half an hour. The albumen coagulating rises to the surface and carries with it mechanically the impurities of the water, which can then be readily removed. The clarified water is now brought into the mash tun so as to raise the temperature of the latter to 65°; a mashing is made, and the whole left to stand for a quarter of an hour; the wort is then drawn off and brought with the remainder of the cold mixture into the vat. From the clear wort thus obtained, a quantity equal to about ten gallons for every hundredweight of bruised malt employed is drawn off and cooled. This liquor—warmer satz—is added to the wort in the subsequent operation of boiling and hopping, by which means a mild and bright beer is said to be produced.

In the Franconian, also known as the Bamberg method, the bruised malt is gradually mixed in the mash tun with water at a temperature of 80°, a mash being obtained of about 60° or 63°. After well stirring up and allowing to stand a short time, the wort is drawn off and boiled, and again brought into the mash tun, by which means the temperature of the latter rises to 75°, again mashed, and the whole allowed to stand for one hour.

The quantity of water used in mashing varies with the district. In Old Bavaria the quantity of water used amounts to about eight times the weight of the malt, while in the Augsburg and Franconian methods the proportion of water is from six to seven times the weight of the malt.

In the Bohemian method four-fifths of the water to be used is brought into the mashing tun, previously heated, in summer to 32° and in winter to 40°; the malt is mashed and stirred, and then the remainder of the water, with the exception of about one-thirteenth part of the whole, which has meanwhile been heated to boiling, is added. After vigorous stirring the thick mash is withdrawn, boiled in the copper during thirty minutes, again returned and stirred. This operation is repeated twice, but the boiling on the second occasion is only continued for twenty-five minutes, and on the third for twenty minutes. The temperature of the mash has by this time reached 75°. The small quantity of water reserved is then heated to boiling, and wort is added to it until it shows signs of turbidity; the mixture is then boiled and added to that in the tun. After standing from half an hour to an hour the wort is drawn off.

The preparation of the wort for the Berlin white beer is described by Stahlschmidt: 36 bushels of crushed malt are mashed with 225 gallons of water at the ordinary temperature, and then scalded with 750 gallons of water sufficiently hot to raise the temperature of the whole mash to about 35° or 40°. From this 200 gallons of clear mash are taken and boiled in the copper with the hops for a quarter of an hour, ½ lb. to 1 lb. of hops being taken for each bushel of malt; it is then returned to the mashing tun and well mashed. 350 gallons are then drawn off, boiled in the

copper, and returned and thoroughly mashed. Finally, another 450 gallons of clear mash is withdrawn, heated to boiling, and then brought into the straining vat, which usually has a wooden straining bottom, generally covered with straw. The interspace between the perforated bottom and the true is also lined with straw. After the clear mash has been brought into the straining vat, the remaining thick mash from the mashing tun is added, taking care that the thick mass of crushed malt is first introduced. The greater part of the hot clear mash collects in the space under the false bottom, and warms the vat and also the added mash, so that the whole is heated to 70°. The mash remains in the straining vat an hour or an hour and a half, and is then clarified, the residue being treated with warm water. Both worts are at once brought into the cooling vessel.

The wort obtained by the infusion method is rich in sugar, consequently yielding an alcoholic beer, which however does not keep so well. By the decoction method, the solution and separation of the wort is facilitated and accelerated by the boiling, but at the same time the action of the diastase is partially impeded, so that the greater part of the starch is only converted into dextrin. A wort is consequently obtained containing much dextrin, and but little sugar and nitrogenous compounds, which yields a weaker kind of beer, but one that keeps well; the dextrin in this beer also determining the retention of carbonic acid, and its gradual evolution.

In whatever way the wort may be produced, a small quantity of extract is always retained in the grains. In order to recover this, after the removal of the upper dough-like mass, fresh water may be added, and the resulting thin wort may be used in the mashing of fresh malt, in the preparation of small beer, or in the manufacture of brandy or vinegar.

The residue, when exhausted as much as possible, contains the husks, nitrogenous constituents, fat, a small quantity of starch, calcium phosphate, and other salts, together with from 60 to 80 per cent. of water.

The strength of the wort varies according to the strength of the beer to be produced; it having a sp. gr. of 1·056 to 1·070 for strong beer, and less, as low as 1·020, for weak beer. The quantity of extract obtained from the crushed malt varies according to the quality and preparation of the raw material. It ranges ordinarily between 55 and 65 per cent. of the weight of the malt; sometimes however it amounts to 70 per cent.

An addition of amylaceous material may be made to the malt during mashing, as the quantity of diastase contained in the malt is so large that it is capable of converting into sugar and dextrin considerably more starch than is contained in the malt itself. In this respect potatoes are especially important, but the starch should be separated before it is added to the mash.

According to Siemens, in the Hohenheim brewery, 100 parts of potato are substituted for 25 parts of malt; and this quantity yields about 15 parts of extract. In the preparation of six barrels of beer, 450 to 500 lbs. of malt are used with 900 to 1000 lbs. of potatoes, or the amount of starch to be obtained from that quantity of potatoes. When the potatoes themselves are used, they are first converted into a paste, which is stirred and washed with fresh water.

About two-thirds of the entire quantity of water to be used, previously heated to 80° or 90°, is brought into the mashing tun; then five-ninths of the malt, moderately dried, is added; next the potato paste or the starch representing it, and the whole is stirred. The temperature of the mash is now brought to 60° or 65°, and maintained at that point until the starch is converted into sugar and dextrin; the mash is then boiled until it becomes clear, which takes place more quickly when starch is used than with potatoes. Meanwhile, the remaining four-ninths of the crushed malt, in a strongly dried condition, is mixed with the remainder of the water in the mashing tun; to this the boiling thick mash is added, and the whole vigorously stirred and then allowed to stand for an hour or an hour and a half. The residuary grains are afterwards again exhausted with hot water.

The constituents of the wort obtained according to different methods are shown in the following table, according to the results obtained by Gschwandler:—

	Decoction	Satz method	In n	With 10 per cent. of starch.
Sugar	4·85	4·37	5·26	5·31
Dextrin	6·24	7·61	6·68	6·23
Nitrogenous matter	0·79	—	—	0·67
Other constituents	0·41	0·95	0·70	0·22

In Germany the boiling and hopping of the wort is mostly carried out in open boilers or pans, which are either used as well for heating the mash, or are placed next the mash tubs. The entire operation has for its objects the concentration of the wort, the coagulation and separation of the dissolved albumin, as well as the mucilage by tannic acid, and the extraction of the essential constituents of the hops.

As before mentioned, the brewing cauldrons are frequently identical with the mash pans; in other cases, however, they are about one-fifth smaller, the shape remaining the same, being more or less shallow flat-bottomed pans of sheet copper or iron. The further the concentration has to be carried the shallower the boiler should be.

In France, and especially in England, closed vessels are frequently used. This method has the advantage that during the boiling less of the aromatic constituents of the hops are lost; the requisite concentration is then often effected by the addition of sugar or molasses. The form of this brewing cauldron is a sphere, but pressed in so as to become convex at the bottom (fig. 692). At the top is a cylindrical dome (*c*),

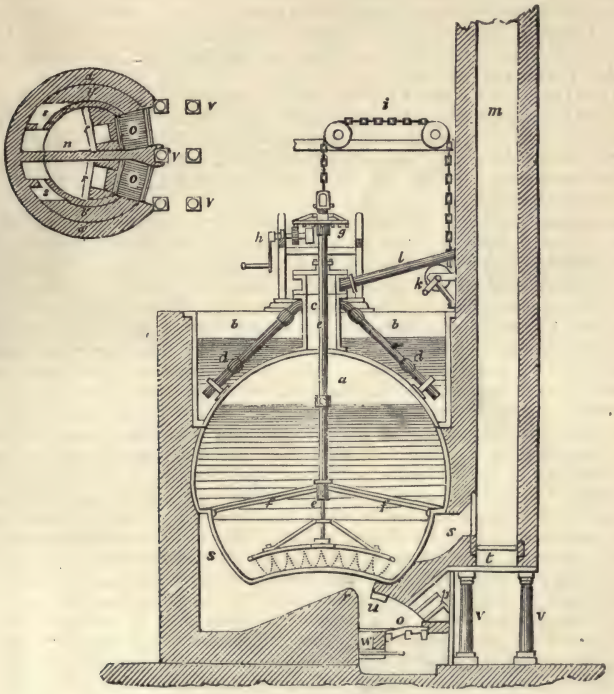


Fig. 652.

from which pass five narrow pipes (*d d*), four of which are carried upwards and lead the steam into the preliminary heating vessel, which is placed directly over the brewing copper, whilst the fifth pipe (*l*) carries the surplus steam upwards into the chimney. Through the dome there passes an axis (*e e*) which can be rotated by means of a toothed wheel (*g*), and to this is attached a stirring apparatus, by which the wort can be kept stirred during the boiling. The fire is placed under the copper, the heated air playing over the bottom and the lower part of the sides of the copper.

The different methods vary in the length of time during which the boiling is carried on. In Bavaria, in the preparation of new beer in open pans, it lasts from an hour to an hour and a half; for lager beer the wort is boiled two to three hours; dark beer is boiled longer than light. In England, where closed vessels are used, the boiling lasts from four to six hours. The scum formed during the boiling is continually removed.

The addition of the hops is made either at the commencement of the boiling or after it has progressed some time, the object in the latter case being that too much of

the aromatic constituents shall not be lost, and that too much of the bitter substance shall not pass into the beer.

It has also been recommended to add a small portion of the hops at the commencement, and the remainder at the end of the operation; or to extract the aromatic constituents of the hops by means of steam in closed vessels, and add the residue to the boiling wort, and the aromatic extract to the cooled wort. Also, a complete extraction of the hops in closed vessels is frequently carried out. In any case, it appears to be the most rational plan not to boil all the hops with the wort during the whole of the operation, because much of the aromatic matter would be thus lost.

The quantity of hops to be added varies according to the length of time the beer requires to be kept. For winter beer 1 to 1½ lbs. of hops are used for 100 lbs. of malt; for lager beer, 2 lbs.; in beer which should keep till October, 3 lbs. In England, the quantity varies between one-twentieth and 4 lbs. of hops to 100 lbs. of malt. The older the hops are, the more it is necessary to use; moreover, old hops are best used for weaker beer.

After the boiling, the wort must be allowed to settle, and it is then drawn off through a perforated chamber called the hop sieve. In order to obtain it as clear as possible, a floating funnel of flexible metal gauze is used, which draws together like a bellows in proportion as the liquor sinks, so that only the uppermost clear liquor flows off through the pipe of the funnel.

The cooling of the wort has for its object the rapid reduction of the temperature of the hopped wort, so as to prepare it for alcoholic fermentation. If the hot liquid were left to cool slowly in the air, there might easily be a formation of lactic and acetic acids, especially between 25° and 50°. It must therefore be rapidly cooled to a temperature of from 10° to 20°, according to the nature of the fermentation to be subsequently effected.

The cooling is effected in large shallow reservoirs, in which the liquors stands from 3 to 4 or at most 6 inches high. The cooling vessels are so placed that a continual change of air takes place above them. The cooling takes from six to twelve hours, and is effected chiefly by the evaporation of the liquor; the strength of the current of air, and especially its dryness, consequently influence the rate of cooling, as also to a less degree does its temperature. During this cooling a further settlement of mucilaginous matter takes place, consisting partially of nitrogenous substance dissolved by the heat, and partially of the compound of tannic acid with mucilage.

Formerly wood was the materia. used in the construction of the cooling vessels, but in consequence of the non-conductivity of wood, and the practical difficulties in repairing and thoroughly cleansing such coolers, they have since been constructed of sheet copper, sheet iron, or cast-iron plates, and recently glass plates have been proposed. Copper is a better conductor of heat than iron, but their difference in this respect is so small as not to be of much importance, especially as the radiating power is at least equally important, and that in the two metals is similar and is greatest when the outside is painted a dull dark colour. Iron has the disadvantage compared with copper that it colours the wort, but this may be prevented by providing the iron with a coating that will impede the direct action of the wort upon it. According to Heiss, this may be done in the following way:—The inner side of the cooling vessel is scoured smooth with sand, and then etched with 7 to 10 per cent. solution of hydrochloric acid. After perfect drying, the etched surface is painted three times with a liquor obtained by digesting finely divided galls in water, with frequent agitation, for twenty-four hours, and decanting. After the third coat is dry, cold water is run into the vessel and allowed to stand for twelve hours, and then an extract obtained by boiling crushed malt and old hops is added. After standing twelve hours the liquor is run off, and the cooling vessel may then at once be brought into use.

As the cooling takes place chiefly through evaporation, of from one eighth to one tenth of the liquid, this is sought to be increased by a change of atmosphere by draughts artificially created by means of ventilators, windmills, and the like, but contact of the wort with too great a quantity of air may easily have an unfavourable influence. The stirring machines which are frequently placed over the cooling vessels have the same object; the augmented contact with the atmosphere being effected by continual renewal of the surface of the liquid. The stirring machines have the disadvantage that they impede the settlement of the turbid portion.

In the course of time, there is deposited upon the sides of the cooling vessels, as well as in the pipes through which the wort is run into them, a crust, known as beer-stone, which washing will not remove. This coating protects the metal of which the apparatus is made from the action of the wort. It contains 64 per cent. of organic matter (including 13 per cent. of protein substances), 29 per cent. of ash free from carbonic acid (chiefly lime), and 7 per cent of water.

Various other cooling arrangements have recently been adopted, such as the cooling

with tinned iron or copper pipes, through which cold water is made to flow, sometimes previously cooled by ice. The method of cooling wort by a current of water has been introduced into England and France. The ice float is also used for the cooling of wort; most frequently, however, in the fermenting vat, and it is especially used in hot summer weather. It consists of a painted sheet-iron tray filled with ice, which is placed in the wort.

The most suitable time for cooling is in the spring and summer months, when dry winds and clear skies promote the evaporation of the wort from the cooling vessels. The situation and plan of the brewery also influences the cooling; evidently the building should be so placed that the coolers are exposed as much as possible to the wind. For this reason breweries situated on high ground (as at Munich), or in airy valleys, yield excellent beer.

Some very important experiments have recently been made by Jicinsky upon the use of the vacuum pan in the beer brewery. According to him, by treating the wort in a vacuum apparatus, concentration and cooling may be combined, and the cooling vessels may be entirely dispensed with. To lower the temperature cold water is added to the wort in the vacuum apparatus, to replace that which has been driven off by the evaporation. As in consequence of the depth of the layer of liquor in the vacuum pan, deposition of suspended substances does not take place, it becomes necessary to filter the wort before it is passed into the fermenting vat. The advantages presented by the use of the vacuum apparatus are: 1. Rapid cooling of the wort in the brewing vat; 2. Saving of space by dispensing with cooling vessels; 3. Simplification of the manipulation, since the wort passes direct from the brewing vat into the fermenting vat; 4. Avoidance of danger of acetification, the wort remaining sheltered from air; 5. Reduction of the consumption of ice.

The fermentation of the wort has for its object, through the action of the yeast as a ferment, to convert the sugar contained in it, together with a great part of the dextrin, into alcohol and carbonic acid, and at the same time to separate dissolved nitrogenous substances in the insoluble form of yeast. According to Lermer's experiments, dextrin alone is not fermented by yeast; but, according to Gschwändler, when dextrin is mixed with sugar, from 22 to 40 per cent. of it undergoes alteration. The manner in which the yeast operates has been particularly described on p. 881.

Occasionally the fermentation takes place in casks; most frequently, however, it takes place in open vats, the fermentation vats, and but seldom in closed vats from which only the resulting carbonic acid can escape. In the latter case the arrangement shown in fig. 693 may be used to prevent access of air to the fermentation vats. It consists of a wooden bung (B), stuck into the cover of the fermentation vat or into the top of the cask, and having a hole bored through its axis opening above into a hemispherical depression. In this lies a ball (C) by which the opening is closed, so that only the gases from the inside can gain a passage by forcing up the ball from time to time.



Fig. 693.

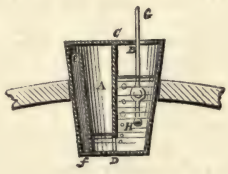


Fig. 694.



Fig. 695.

Another arrangement, having the same purpose, is shown in fig. 694 in section. The space (A) communicates through the pipe (*f*), with the interior of the vessel. Between the spaces A and B is a partition (C D), which does not reach quite to the bottom, so that the water placed there can pass from side to side. As soon as gas enters through the pipe (*f*), it exercises a pressure upon the surface of the water in A, until it can escape under the partition at D. The level of the water in B is consequently raised and with it the float (H G), indicating the progress of the fermentation. A float of the simplest construction is represented in fig. 695. H G' is an iron wire and *a* is a piece of cork by which it is floated.

After trying the most diverse materials, in order to replace wood in the fermentation vats, because it becomes strongly impregnated with the fermenting liquid and very difficult to purify, experiment has lately been made with glass. Brickwork reservoirs are covered with large glass plates, the joints being closed with good cement and having a substratum of water glass.

The place where the fermentation is carried on should have an equable temperature of from 8° to 12°. Ordinarily an arched vault is chosen, which must be kept very clean, because impurities would have an injurious influence upon the keeping property of the beer prepared in it.

The nature of the fermentation is determined by the character of the yeast employed and the temperature at which the liquid is maintained during the fermentation. It is either of the kind called surface fermentation or sedimentary fermentation. Surface fermentation is produced by ordinary yeast, which is used in those cases where it is desired to prepare rapidly drinkable beer and to conduct the fermentation within the ordinary range of temperature. Wort which contains so much sugar that sufficient alcohol is formed by a partial fermentation is also fermented by surface yeast. This kind of fermentation takes place most readily and with the greatest rapidity, for which reason it is employed in working wort that is not completely fermentable with ease, as is the case with wort that has been boiled for a long time or has been prepared from highly roasted malt.

In carrying out surface fermentation the wort is brought to a temperature ranging between 12° and 16°, in the fermenting tun, and mixed with surface yeast from a previous operation, in the proportion of from 2 to 4 lbs. to the hundred gallons. The rapidity with which fermentation commences depends upon the external temperature. At the commencement a white froth collects at the surface of the liquid and rapidly increases, moving in concentric rings from the circumference to the centre. This froth consists chiefly of resinous constituents from the hops; it has on this account a very bitter taste, and is removed so as not to become mxed with the yeast afterwards produced. Subsequently there is formed a light yellowish froth, interspersed with large bubbles, which constitutes the new yeast, or barm, that is formed from the nitrogenous constituents of the wort and a part of the sugar. During this formation of yeast carbonic acid gas is abundantly evolved, and by adhering to the particles of yeast separated in the liquid floats them to the surface, forming the surface yeast, while another portion is deposited as bottom yeast. After the lapse of from four to eight days the rapid evolution of carbonic acid ceases and the first stage of the fermentation is at an end. The product in this condition is called young beer. A further fermentation that progresses very slowly, and is called the after fermentation, then commences under the influence of the bottom yeast that is mixed with the beer. This fermentation is generally allowed to go on in casks, or smaller tuns, having only a small opening through which carbonic acid can escape and the yeast froth can run away. As soon as the froth becomes white the beer is ready to be transferred to the store casks, which are securely closed when filled. In these casks a second after fermentation takes place, which has the effect of saturating the beer with carbonic acid and keeping it in a fit state for consumption. The beer must be drunk while this fermentation is still in progress. Its capability of being preserved depends upon a continuance of this fermentation and upon the temperature of the store cellar, which should be as cool as possible. The size of the casks is also of some influence, for the larger they are the less is the beer affected by changes of temperature in the store cellar.

In order to make drinkable beer in a short time the wort is brought to a temperature of from 16° to 24°, mixed with some yeast, and immediately after the commencement of the fermentation run into casks, where it rapidly ferments within the space of one or two days, the yeast escaping out of the bunghole meanwhile. The beer is then drawn off into small casks where the after fermentation takes place. After a few days the beer can be drawn off into bottles in which it becomes impregnated with carbonic acid by the progress of the after fermentation.

The sedimentary fermentation progresses much more slowly than the surface fermentation, and it is specially employed in the preparation of beer that is required to be kept. Bavarian beer is generally prepared in this way. The wort is cooled down to a temperature ranging from 6° to 10° and is mixed with from ½ to ¾ per cent. by measure of bottom yeast. After about twelve hours a light froth appears at the surface forming rings diminishing towards the centre. Evolution of carbonic acid soon commences, but the gas given off is not sufficient to lift the yeast to the surface, and on account of its remaining at the bottom of the liquid it is termed bottom yeast. At the end of from seven to ten days the chief fermentation is completed; the beer is then run off into casks in which the after fermentation takes place. During this stage some frothy yeast is produced which runs away from the bunghole and is removed.

When the beer has become clear the casks are closed, and the slow fermentation commences, during which sufficient carbonic acid is formed to make the beer sparkling.

It is very essential that the place where this slow fermentation goes on, and in which the beer is kept, should be kept very cool. The temperature of the store cellar

especially should not exceed 5°, and if necessary it should be kept cool by means of ice.

During this fermentation the amount of extract decreases, and at the same time the specific gravity of the beer diminishes progressively, so that the progress of the fermentation may be judged of from the specific gravity of the beer.

If the various operations are not properly carried out, the beer occasionally clears with such difficulty that it has to be assisted by artificial means. The best clarifying material is isinglass, the dried swimming bladder of several species of sturgeon. This is soaked in water for twenty-four hours, and afterwards dissolved by heating it with 16 or 20 parts of weak spirit, beer, or water. This preparation is thoroughly mixed with a portion of the beer to be clarified, and the mixture is added to the remainder of the beer. After some time the isinglass settles to the bottom, carrying with it the suspended particles, and the beer becomes clear. About 4 or 5 parts of isinglass are used to 100,000 parts of beer. The action of this substance depends upon the peculiar structure of the tissue of the bladder, which consists of a fine network of small fibres that swell to 100 times their original volume when soaked in water or weak spirit, especially under the influence of slight acidity. When this voluminous jelly is mixed with the beer, the fibres are again contracted under the action of the alcohol, and the network closing upon the turbid particles in the beer carries them to the bottom.

The Berlin white beer is frequently clarified with isinglass that has been swelled with tartaric acid before being set to ferment. The tartaric acid then increases the peculiar sour taste of that beer.

Fleck recommends the addition of glycerin to the wort before it comes into the fermenting vat, in order to impart to the beer a full flavour, and to remove the bitterness arising from the use of a large quantity of old hops. According to the quantity of hops used, ½ to 1 part of glycerin is added to 100 parts of beer; the glycerin is shaken with four times its volume of cooled beer, and this mixture is distributed through the fermenting vat before the yeast is added. The glycerin is not added at an earlier stage because too much of it would be evaporated with the vapour of water during the boiling and cooling of the wort.

The investigations of Pasteur have thrown much light on the life history of the yeast plant or plants; and, although all the inferences he has drawn from his observations have not met with full acceptance, there can be no doubt that his researches will greatly influence the future of beer brewing.

Pasteur starts with the admitted fact that there exists a close relation between the facility with which beer wort or the finished beer undergoes alteration and the processes adopted in its manufacture. This is practically indicated in the rapid reduction of the temperature of the wort from about 50° to below 20° in order to avoid the lactic and acetic fermentations that readily occur between those points. In seeking for the cause of the changes which spoil the beer he finds that they are always coincident with the development of microscopic organisms foreign to the nature of true beer yeast. The organisms act as ferments and their multiplication is always accompanied by the production of acid, putrid, viscous, or bitter substances which render the beer unpalatable; they are therefore designated as ferments de maladie. Most of them, if not all, differ considerably in size and shape from the spherical germs of beer yeast. The organisms present in turned beer are simple or articulated filaments, about one-thousandth of a millimetre in diameter, which, when very strongly magnified, are seen to consist of a series of short rods. The organisms in lactic beer are small particles, slightly contracted in the middle, of rather greater diameter than the preceding, generally isolated, but sometimes joined in chains of two, three, or more. The organisms in putrid beer are vibrios, moving more or less rapidly according to the temperature; these make their appearance in the wort more readily than in the beer. The organisms in viscous beer consist of strings of nearly spherical granules.

Tart or acetic beer contains chaplets of articulations of *Mycoderma aceti*, extremely similar in appearance to those of the lactic ferment, but differing very much in their physiological functions. All these are more or less filamentary, and, according to Pasteur, their presence in beer is an infallible sign that deterioration has either commenced or is impending. They have their origin in germs deposited from the air in the beer or on the vessel during the operations, or present as a contamination with the beer yeast used. These organisms may, under certain conditions, increase so as to materially affect the nature of the deposit of yeast, sometimes even to the extent of entirely displacing the alcoholic ferment; hence the necessity that arises in a brewery occasionally of getting a supply of fresh yeast from another establishment. Pasteur has also found that the absence of these *ferments de maladie* is coincident with the production of an unalterable beer.

The predominance of one or other of these ferments under particular conditions has given rise to the belief that they are all modifications of the same vegetable organism, brought about by the media in which they occur. This, however, is denied by Pasteur, who maintains that under no conditions is one form converted into another, such as, for instance, the beer ferment into the lactic ferment. The explanation is found by him in the greater appropriateness of certain liquids for particular growths. Thus an acid liquid, such as the must of grape, may have deposited in it simultaneously the spores of mucedines, and the germs of bacteria, leptotrices and vibrios; but the latter would be hindered in their development, if not killed, by the acidity of the liquid, so that they would not be met with in the adult state. Most of the moulds, on the contrary, flourish in acid liquids, excluding all other growths. But if the must when fresh be saturated with carbonate of lime, the reverse conditions obtain; bacteria, lactic ferment, and butyric vibrios invade the liquid to the exclusion of moulds, which only languish in alkaline solutions. When one kind of growth is established it hinders for the time all others, by appropriating all the alimentary material, especially the oxygen.

It is to be noted, however, that a period of vigorous growth of a particular ferment is often followed by a gradual slackening, and finally a cessation in the development, caused by the exhaustion of the necessary aliment from the liquid, which may thus become favourable for the growth of another ferment.

This difference in the suitability of certain liquids for the development of particular growths Pasteur proposes to utilise for the elimination of objectionable ferments present in beer yeast, by repeated cultivations of the yeast in liquids unfavourable to their development.

Although, according to Pasteur, no other fungoid vegetation is capable of being converted, even under the most favourable conditions, into beer yeast, some of them, such as *Penicillium glaucum* and *Aspergillus glaucus*, are capable of acting to a certain extent as alcoholic ferments. If these fungi are growing in a saccharine liquid in contact with atmospheric air, they appear to effect a complete combustion of the sugar by means of the free oxygen contained in it; but if they be submerged, so as to deprive them of a supply of oxygen, they then appear to act as alcoholic ferments, by decomposing the sugar with formation of alcohol, carbonic acid, and other undetermined substances, possibly varying with the plant acting as a ferment. But in this case, with the moulds mentioned a marked alteration in their shapes takes place; the growth becomes languid from want of oxygen, the mycelium becomes thickened, and instead of appearing in long filaments takes the form of chains of more or less ovoid cells, and after a time development entirely ceases. Pasteur designates this class of fungoid growths, which are not capable of flourishing if deprived of access of air, aerobies, and those that can live without a supply of atmospheric oxygen, or the true ferments, he calls anaerobies.

As elsewhere stated, two kinds of fermentation are recognised in the beer industry, superficial fermentation, which is that almost exclusively at present practised in this country, and bottom fermentation, which is largely practised on the continent. The ferments which are used to produce these fermentations differ but little in respect to their development; the cells of bottom yeast are slightly smaller, a little more oval, and have a perceptibly less ramification in the germination than those of surface yeast. But the most marked difference is that from which they take their respective names; whilst one is floated to the surface of the liquid, and kept there by carbonic acid gas evolved, the other remains at the bottom of the vessel, and, as might be expected from what has been said above, its action, remote from the air, is much the slowest of the two. Moreover, there is a great difference in the temperature at which they each manifest their activity, the superficial fermentation being usually carried on at a temperature of 16° to 20°, whilst the bottom fermentation is never carried on above 10°, and preferably at from 6° to 8°, a temperature at which the superficial yeast would be without action. Notwithstanding these differences it is considered by many that these two ferments are identical, and may be transformed one into the other under favourable conditions. This is contrary to the opinion of Pasteur, who admits, however, that probably they present an example of modifications that have become hereditary by prolonged cultivation, since beer cannot be said to have a natural ferment in the same sense as the juice of the grape.

The contact of an excess of atmospheric air exercises an important influence upon the phenomena of fermentation. In such a case the yeast vegetates like a mould, and there may even be a considerable development of yeast cells upon the surface of a saccharine liquid before any formation of alcohol takes place, the quantity of alcohol produced in relation to the weight of yeast present being always in inverse proportion to the quantity of free oxygen available for the life of the plant. On the other hand the condition in which the yeast cells are most capable of developing and multiplying

within the fermentescible liquid is while they are still very young, and still under the influence of the active vitality due to contact with free oxygen, which possibly they may to some extent be able to store up within them. Upon these grounds Pasteur refers the phenomenon of tumultuous fermentation to the presence of excess of free oxygen in the fermenting liquid.

It will be evident that, if the foregoing views of Pasteur are correct, it will be important that not only should pure yeast be used, but that the beer should be protected during its manufacture from contamination with foreign ferments by the deposition of spores floating in the air. For this purpose he has devised some apparatus in which the cooling and fermentation would take place in contact only with filtered air. At present this experiment has not been adopted to any extent. Pasteur, however, does not look upon all the foreign ferments as injurious, but considers that some of them might probably be utilised in the production of different flavoured beers. For instance, he has recognised that an admixture of a special ferment that has been named after himself, *Saccharomyces Pastorianus*, yields a beer that has a distinctly vinous flavour.

The relative amounts of dextrin and sugar present in the wort have an important influence upon the rapidity of the fermentation, and consequently the durability of the beer produced. Sugar enters into fermentation readily, and this fermentation progresses rapidly, and cannot easily be checked at ordinary temperatures until it has run its course, when carbonic acid ceasing to be evolved the beer becomes flat and more liable to acetification by absorption of oxygen from the air. Dextrin, on the contrary, ferments but sluggishly, especially at low temperatures, so that its fermentation is prolonged after all the sugar has been decomposed, giving rise to a continual development of carbonic acid, and thus contributing to the permanence of the beer. Hence for the production of a beer for early and rapid consumption a large proportion of sugar in the wort is eminently suitable; whilst for a beer that requires to be kept a considerable time dextrin should predominate. Moreover the time of the year should also be considered, as whilst in the summer time a little more dextrin would be useful as a clog to too rapid fermentation, in winter it might have a deleterious influence and favour viscous fermentation.

In Yorkshire and other of the northern counties of England, a method of fermentation is adopted known as the stone square system, which is alleged to be not only economical in its working but capable of producing a very full beer in proportion to the original gravity of the wort used. The square consists of an outer jacket or shell, built of four massive stone slabs fixed upon another slab that forms the bottom, and, within this, the wort cistern, similarly formed of stone slabs, and of a size that allows a clear space of about 2 inches between its walls and those of the jacket, but 2 or 3 inches higher. Over this is a covering slab having three holes in it, and supporting another stone cistern called the yeast back, which is large enough to hold all the yeast formed during the operation. The principal hole in the cover is surrounded by a stone ring about 6 inches high; a smaller hole (about 2 inches in diameter) is furnished with a valve, and fitted on the under side with a long tin pipe, reaching to within 2 inches of the bottom of the wort cistern; a third hole, with a plug, is used for running off the yeast. The wort cistern is provided with one or more cocks passing out through the sides of the jacket and used for drawing off the beer for racking. There are also the necessary pipes and cocks for supplying the interspace between the jacket and the wort cistern with hot or cold water as it may be required to control the temperature of the wort.

The wort is run into the cistern until it rises through the smaller opening of the cover, the valve of which is left open, into the yeast back to a height of 2 or 3 inches; the valve is then closed. Sometimes the yeast is added as the wort is run in, and the whole is left undisturbed until the fermentation is finished, when the yeast is run off, and the wort having become perfectly still is ready for racking. But generally the yeast is added after the wort is in the square, a comparatively small quantity being used. Fermentation commences in about 12 hours, and when in full vigour the yeast head and the wort in the yeast back are well roused together, and the valve being opened, the mixture is run through the tin pipe to the bottom of the wort cistern. The valve is then closed, and after an interval which must be decided by the judgment of the operator some wort is pumped up into the yeast back by means of a hand-pump passed through the principal opening of the cover to nearly the bottom of the wort cistern. The fresh head and this wort are roused together, and run down through the tin pipe as before, and these operations are repeated until the degree of attenuation desired is obtained. The yeast is then allowed to separate from the beer, which it does completely in the course of a few hours, discharging itself into the yeast back, whence it is removed, and the beer after standing until bright is ready for racking.

The temperature found most suitable for this method is from 15° to 16° at the commencement, with a maximum of 70°. When the latter temperature is reached cold water is admitted into the jacket to prevent a further rise.

Beer Analysis.—The percentage of carbonic acid in beer may be determined by treating a known quantity of the beer with baryta water, filtering off the precipitate, and drying and washing it. The precipitate thus formed is not pure barium carbonate, therefore the carbonic acid must be determined by any of the known methods. In treating with baryta water care must be taken to exclude atmospheric air.

Another method of determining the quantity of carbonic acid present in beer consists in heating a known quantity of beer to 40°, the vessel containing the liquid being shaken to liberate the carbonic acid; upon again weighing, the loss in weight represents the carbonic acid disengaged.

For the determination of the total amount of extract, a known quantity of beer is weighed in a Liebig's drying tube, then evaporated in a stream of dry air over a salt or oil bath at a temperature of 100° or 120°, the application of heat being continued so long as loss of weight takes place. The weight of the residue represents the total extract of the sample of beer taken. Another method consists in evaporating a known quantity of beer in a platinum dish over a water bath, then drying the residue at a temperature of 100° or 110° and weighing; in this operation it is advisable to mix the beer with a weighed quantity of sand before evaporating.

An easier and simpler method of testing beer is Fuch's hallimetric test, based upon the fact that 100 parts of water dissolve 36 parts of common salt, or 1 part in 2·778, and that a liquid dissolves less salt the greater the quantity of alcohol and extract it contains. Two tests are therefore necessary: 1,000 grains of beer are weighed off, and boiled down in a flask to one-half or one-third its volume, by which the whole of the carbonic acid, the alcohol, and a part of the water are driven off; the liquid is then mixed with water so as to make it up again to exactly 1,000 grains. 360 grains of salt, as nearly as possible of the same degree of fineness, is added to this liquid, and the whole shaken. A portion of the salt will remain undissolved, and in order to determine the quantity the whole is poured into an instrument termed the hallimeter (fig. 696), which consists of a glass tube closed at one extremity, the upper and open part being wide and cup-shaped, the lower portion narrower. The salt deposits in the lower tube, and when the particles are small and uniform (which may be secured by sifting) the volume corresponds to a definite weight. The weight of the undissolved salt is easily determined from its volume, since the graduations on the lower limb of the hallimeter correspond each to one grain of salt. Thus, for instance, if 21 grains of salt remain undissolved and 339 grains have been dissolved, the 1,000 grains of boiled beer contain 339 × 2·778 or 942 water and 58 grains of extract.



Fig. 696.

In a second experiment 1,000 grains of beer are treated with 330 grains of salt, heated over a water bath to 35°–40°, and freed from carbonic acid by shaking. The quantity of carbonic acid is ascertained from the loss of weight. The salt added will not dissolve completely in the beer, and the weight of the undissolved portion is ascertained by measuring as above described. The quantity of salt dissolved multiplied by 2·778 gives again the quantity of water, and the difference the quantity of extract and aqueous alcohol. The amount of extract having been ascertained in the first experiment, the difference gives the quantity of aqueous alcohol contained in the beer. However the amount of absolute alcohol in the aqueous alcohol is not constant, and since it would contain relatively more water in proportion as the beer is rich in alcohol, the table II. must be referred to.

An example will serve to explain the method of calculation. 1,000 grains of fresh beer, shaken up with 330 grains of common salt, lose 2 grains in weight = carbonic acid. There remains undissolved 22 grains = 144 grams of extract and aqueous alcohol (table I. B). In the above experiment the boiled beer left 21 grains of salt undissolved, 360 having been employed; hence the beer contains, according to I. A, 58 grains of extract, and accordingly 144 − 58 = 86 grains of alcohol. 100 parts of the beer therefore contain—

Carbonic acid	0·2
Extract	5·8
Alcohol	4·7
Water	89·3
	100·0

Column A in Table I. gives the quantity of extract contained in the wort or boiled beer, calculated from the residue remaining from 360 grains. Column B of the same

table shows the quantity of extract and aqueous alcohol in unboiled beer, corresponding to the salt residue from 330 grains. The percentage of absolute alcohol in this aqueous alcohol is then found by reference to B.

TABLE I.

Salt residue	Extract A	Extract and alcoholic contents B	Salt residue A	Extract A	Extract and alcoholic contents B	Salt residue	Extract A	Extract and alcoholic contents B
0	—	83	14	39	122	28	78	161
1	—	86	15	42	125	29	81	164
2	—	87	16	44	128	30	83	167
3	—	92	17	47	131	31	86	169
4	—	94	18	50	133	32	89	172
5	—	97	19	53	136	33	—	175
6	—	100	20	56	139	34	—	178
7	—	103	21	58	142	35	—	181
8	22	106	22	61	144	36	—	183
9	25	108	23	64	147	37	—	186
10	28	111	24	67	150	38	—	189
11	31	114	25	69	153	39	—	192
12	33	117	26	72	156	40	—	194
13	36	119	27	75	158			

TABLE II.

Aqueous alcohol A	Absolute alcohol B	Aqueous alcohol A	Absolute alcohol B	Aqueous alcohol A	Absolute alcohol B	Aqueous alcohol A	Absolute alcohol B
39	21·5	67	37·6	95	52·1	123	66·5
40	22·0	68	38·1	96	52·6	124	67·0
41	22·6	69	38·6	97	53·1	125	67·6
42	23·2	70	39·1	98	53·7	126	68·1
43	23·7	71	39·6	99	54·2	127	68·6
44	24·3	72	40·2	100	54·7	128	69·1
45	24·8	73	40·7	101	55·2	129	69·6
46	25·4	74	41·2	102	55·7	130	70·1
47	25·9	75	41·7	103	56·2	131	70·6
48	26·5	76	42·2	104	56·8	132	71·3
49	27·0	77	42·8	105	57·3	133	71·8
50	27·6	78	43·3	106	57·8	134	72·3
51	28·2	79	43·9	107	58·3	135	72·8
52	28·7	80	44·3	108	58·8	136	73·3
53	29·3	81	44·8	109	59·3	137	73·8
54	29·8	82	45·4	110	59·8	138	74·3
55	30·4	83	45·9	111	60·4	139	74·8
56	30·9	84	46·4	112	60·9	140	75·3
57	31·6	85	46·9	113	61·4	141	75·8
58	32·2	86	47·4	114	61·9	142	76·3
59	32·8	87	48·0	115	62·4	143	76·8
60	33·4	88	48·5	116	62·9	144	77·3
61	34·0	89	49·0	117	63·4	145	77·8
62	34·6	90	49·5	118	63·9	146	78·3
63	35·2	91	50·0	119	64·5	147	78·8
64	35·8	92	50·5	120	65·0	148	79·3
65	36·4	93	51·1	121	65·5	149	79·8
66	37·0	94	51·6	122	66·0	150	80·3

To determine the Sugar and Dextrin.—A weighed quantity of beer is evaporated to a syrupy consistency, and the residue treated with alcohol to dissolve out the sugar, this operation being repeated until all the sugar has dissolved; the alcoholic extracts

are collected and heated to dryness, and the sugar dried and weighed. The dextrin is determined by diluting with water the residue insoluble in alcohol and boiling with sulphuric acid, by which the dextrin is converted into sugar, and may be determined by means of Fehling's copper solution.

Determination of the Alcohol.—Besides the hallimetric test, a method often employed consists in placing a weighed quantity of beer in a flask connected with a Liebig condenser, and distilling off about one-third of the beer.

By means of Geissler's vaporimeter the alcoholic contents of any aqueous liquid is determined from the tension exhibited by the liquid when heated to 100°. When beer is to be tested in this way it requires previously treating with lime, so as to remove from it carbonic acid.

The tension of a liquid thus treated is of course greater in proportion to its alcoholic contents. The apparatus consists of a glass vessel for holding the beer or other liquid to be determined, and which can be heated by steam to 100°. The vessel is connected with the short arm of a doubly limbed tube, the long limb of which dipping in mercury shows by means of suitable graduations the tension which corresponds with the alcoholic contents of the liquid.

ACETIC ACID.

History.—Acetic acid was known in the form of vinegar at a very remote period, the Jews, Greeks, and Romans having been acquainted with its medicinal properties as well as its domestic uses. Dioscorides and Pliny also treat of the application of vinegar in medicine. The alchemists first obtained acetic acid by distillation, and in the eighth century Geber prepared it in a concentrated form. Basil Valentin was probably the first chemist to prepare acetic acid from an acetate, using crystallised verdigris and basic acetate of copper. The production of pure and concentrated vinegar was improved at the commencement of the eighteenth century by Stahl, who showed that the concentration of vinegar was to be accomplished by freezing out the water, and that the strong acid could be obtained by distilling acetate of potash or sugar of lead with sulphuric acid. The production of acetic acid by dry distillation of vegetable substances was mentioned by Glauber in 1648, but H. Kopp is of opinion that wood vinegar was known anterior to that time.

Occurrence.—Acetic acid occurs in the juice of various plants, partly in the free state, and partly in combination with lime or alkalies. It is a normal constituent of many animal liquids, and it has been observed in sweat and in putrefying animal and vegetable substances. It occurs also as a product of the oxidation of alcohol, and the alteration of dilute alcoholic liquids, such as wine, beer, etc., which become sour when exposed to contact with atmospheric air, consists essentially in the conversion of the alcohol they contain into acetic acid. This phenomenon, which is termed acetous fermentation, is promoted by the presence of a peculiar fungus or mildew, which is readily developed in such liquids. Acetic acid likewise occurs among the products obtained by the action of heat upon wood and other analogous materials.

Composition.—Pure acetic acid has the formula $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$, and is the hydrate of an oxygenated radical acetyl, C_2H_3O, which is derived from alcohol by the substitution of oxygen for part of the hydrogen in the ethyl, as shown by the following equation:

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + 2O = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + H_2O.$$

The anhydrous acid or acetic anhydride has the formula $\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$.

Characters.—At ordinary temperatures acetic acid is a pungent and colourless liquid, which solidifies by cooling to a crystalline mass. The solid acid melts at 16°, but the liquid must be cooled far below that point to make it solidify. A very small quantity of water lowers the solidifying point very considerably. The boiling point is about 119°, and the vapour is inflammable. Acetic acid has a specific gravity of 1·063 at 12·5° ; it is miscible in all proportions with water ; the gravity first increases and then decreases as shown in the following table. For this reason a solution containing 54 per cent. of pure acetic acid has the same specific gravity as the pure acid.

Acetic acid per cent.	sp. gr.	Acetic acid per cent.	sp. gr.
100	1·0635	35	1·046
90	1·0730	30	1·040
80	1·0735	25	1·034
70	1·070	20	1·027
60	1·067	15	1·022
50	1·060	10	1·015
45	1·055	5	1·007
40	1·051	1	1·001

Consequently specific gravity does not indicate the amount of acetic acid. It would be better, at least with an acid which is not too dilute, to estimate its strength by the solidifying point.

The following table by H. Rüdorff gives the solidifying points of acetic acid of different strengths:

Water, per cent.	Solidifying point.	Water, per cent.	Solidifying point.
0·0	16·7° C	7·407	6·25° C
0·497	15·65°	8·257	5·3°
0·990	14·8°	9·090	4·3°
1·477	14·0°	9·910	3·6°
1·961	13.25°	10·714	2·7°
2·912	11·95°	13·043	−0·2°
3·846	10·50°	15·324	−2·6°
4·761	9·4°	17·355	−5·1°
5·660	8·2°	19·354	−7·4°
6·542	7·1°		

As sulphuric acid exerts a considerable influence on the solidifying point of acetic acid, no value can be attached to the solidifying point when this acid is present.

Acetic acid is also miscible with alcohol, and with ether in all proportions; in many ethereal oils it is insoluble, and it is the more insoluble as the hydration of the acid increases.

A good test of the purity of acetic acid is the degree to which lemon oil dissolves in it; the pure acid should entirely dissolve one-tenth of lemon oil. Gelatin, fibrin, albumin, camphor, and gun cotton are dissolved by cold acetic acid. Acetic acid is expelled from its salts by sulphuric acid, hydrochloric acid, or phosphoric acid, but it decomposes carbonates and expels many volatile organic acids from their respective salts.

The salts of acetic acid are variously affected by heat. Some lose a portion of the acid, others yield acetone.

Acetic anhydride is a liquid boiling at 117·5°; its specific gravity is 1·0799. It combines very energetically with water, forming the hydrate or hydrogen salt called acetic acid, the corresponding compounds of the oxide with basic oxides being called acetates.

An aqueous solution containing from 3 to 10 per cent. of acetic acid is known by the name of vinegar, and used for domestic purposes. It also contains small quantities of alcohol, ethereal oils, sugar, dextrin, colouring matters, and soluble salts. The nature of the other constituents, which impart the characteristic smell and taste, depends upon the kind of material the vinegar has been made from. Wine vinegar has a better flavour than the vinegar made from brandy or beer.

Preparation.—The principal source of acetic acid is the aqueous liquid obtained, together with tar and combustible gases, when wood is subjected to destructive distillation.

The nature of the product obtained in this way depends upon the kind of wood operated upon, and the temperature at which the operation is conducted.

The best wood for the purpose is that of foliaceous trees grown on dry soil. The wood of pine and fir trees is not so productive.

According to the experiments of Peters the following results are obtained from various kinds of wood:

	Wood vinegar p. cent.	Acetic acid p. cent.	Tar p. cent.	Carbon p. cent.
Beech	48·3	6·1	4·9	23·9
Birch	48·0	5·7	6·0	21·1
Alder	47·7	3·9	5·2	24·0
Oak	47·6	5·4	6·4	24·9
Ash	46·8	4·0	6·4	23·7
Copper beech	46.3	5·3	6·2	23·8
Lime	46·2	6·3	8·9	21·8
Fir (Scotch)	44·9	2·7	10·1	28·0
Willow	43·4	6·3	6·2	23·6
Larch	42·8	2·9	9·5	22·6
Maple	42·2	5·5	6·2	26·3
Silver fir	40·9	2·4	11·0	26·1
Pine	40·6	2·8	9·4	28·3

In England the wood for this purpose is obtained from the oak, beech, birch, hawthorn, and apple trees, less frequently from the hazel, alder, ash, and maple, and seldom from the poplar, elm, and pine. Chapman has stated that the oak, which is almost always taken stripped of its bark, yields the best wood vinegar, but a friable charcoal which has a small bulk. Beech wood yields very good charcoal, together with a considerable

quantity of wood spirit and creasote. Birch, hawthorn, and apple trees give very pure wood vinegar.

The roots of trees yield a very good product, but they are difficult to cut up, so as to be suitable for distillation only. They must not be rotten, nor must rotten wood of any kind be used for distillation.

Next to the kind of wood, the temperature employed in the distillation is of importance as regards the yield. Chapman obtained results varying from 13 to 27 per cent. of charcoal, according as he used a higher or lower temperature in distilling oak sawdust.

The higher the temperature the less charcoal is obtained, A better yield is obtained by slowly increasing the temperature; the quicker the temperature is raised the less liquid products are obtained, but more gaseous products are produced. Slow carbonisation is therefore to be recommended.

The kind of apparatus to be used varies according to the nature of the raw material. For heavy wood which can be brought in logs—the refuse from dockyards of timber, etc.—it is customary to use a horizontal cast-iron retort, somewhat similar to a gas retort. It is from 7 to 10 feet long and $2\frac{1}{2}$ to $3\frac{1}{2}$ feet in diameter. A vertical cylindrical vessel would equally serve the purpose. The retort is fed with the logs, and the cover having been fitted on, the required heat is obtained from a fire underneath.

The volatile products escape through an outlet in the upper part of the cylinder, and the charcoal remains behind. The distilled products are passed through a condenser surrounded with cold water, into a receiver where the tar, water, vinegar, and wood spirit are condensed, and the noncondensable gases escaping through an opening in the lower part of the condenser are generally carried to the furnace, so as to effect a saving of fuel, as these gases consist of marsh gas, olefiant gas and other combustible gases. At the end of the distillation, which in a large retort will take about twenty-four hours, the hot charcoal is as quickly as possible placed either in a closely fitting sheet-iron vessel or in a well-closed brick chamber.

When light wood and irregularly sized pieces are to be worked up with small branches, brick ovens with direct or indirect firing are advantageously used instead of retorts. The oven is either closed with an arch or open at the top, in which case, after the wood has been placed in the oven, it is covered with a layer of earth and turf. In Reichenbach's oven the heating is effected by means of iron tubes passing through the oven, and heated to a red heat by a fire outside.

Halliday has constructed a very excellent apparatus for the distillation of sawdust and such like wood refuse. It is a horizontal cast-iron retort, heated externally by a furnace. On the front end is a filling hopper, in the cylindrical neck of which a screw turns to regulate the filling. In the retort, also, another screw revolves, and gradually drives the sawdust from the feeder through the retort. In this way perfect carbonisation is effected.

The volatile products are led off and condensed, and the charred residue is allowed to fall from the end of the retort into an air-tight iron box, or into water, in which case, the discharge pipe dips into the water.

Treatment of the Crude Distillate.—The crude distillate obtained by the dry distillation of wood is allowed to rest for some time in a reservoir where it separates into two layers, the upper one containing, besides much water, the acetic acid and wood spirit, while the lower layer consists of tar. The aqueous layer having been drawn off as clear as possible, and filtered through sand, is subjected to fractional distillation in a copper retort, heated by steam pipes. The wood spirit, coming over in the first fifth of the distillate, is again fractionated over quicklime, and finally treated with a little sulphuric acid to remove the ammonia. It still contains such impurities as acetone, empyreumatic oils, ethers, etc. After the removal of the spirit the distillation is continued, and the wood vinegar distilling off is condensed and collected in a fresh receiver. The tar remaining in the still is run off by a cock from the bottom.

In many works the acid is neutralised with lime before distilling off the wood spirit. In this case the residue in the retort contains acetate of lime; iron instead of copper retorts can be employed in working by this method.

The crude acetic acid is purified by first neutralising with lime or soda, either before or after distillation. When the liquor has settled it is drawn off clear and evaporated until it crystallises. The calcium or sodium acetate thus obtained is separated from the mother liquor, dried between 230° and 250° C., and distilled with sulphuric acid to obtain pure acetic acid. Acetate of lime has previously to be treated in solution at a specific gravity of 1·2, with powdered sulphate of soda, so as to form the sparingly soluble double sulphate of lime and soda, and leave in solution the acetate of soda, which can be recovered by crystallisation.

Hydrochloric acid might be employed to decompose the acetate of lime instead of converting the calcium salt into sodium acetate, but care must then be taken to avoid using any great excess of hydrochloric acid or the distillate would be impure.

When the crude product is neutralised with lime before distilling off the wood-spirit, the residual liquor is evaporated down and the dry mass is heated until oil and tarry vapours are no longer disengaged.

Manufacture of Vinegar.—The conversion of the alcohol in beer or wine into acetic acid is a phenomenon familiarly known as the acetous fermentation, and the dilute solution of acetic acid, known as vinegar, is usually made in this way. Various dilute alcoholic liquids, such as wine or fermented malt infusion, are employed for this purpose; the change that takes place consisting in oxidation of the alcohol they contain, and being associated with the development of the mildew fungus called *Mycoderma aceti*, ordinarily known as mother of vinegar, or vinegar mould, which forms a coating upon the surface of the liquid undergoing acetous fermentation. A very small quantity of this fungus placed on the surface of a dilute alcoholic liquid will in a short time convert the alcohol into acetic acid. If the alcoholic liquid contain albuminous substances and alkaline phosphates, as is the case with wine and beer, the fungus rapidly multiplies and the formation of vinegar is accelerated.

The conversion of the alcohol into acetic acid always takes place at the surface of the liquid and continues only so long as the fungoid growth floats upon the liquid. When it sinks below the surface out of contact with the air, the action ceases. It is still a matter of doubt whether the action of the *Mycoderma aceti* is physiological or merely physical. The fact that it can also oxidise acetic acid into carbonic acid and water speaks in favour of a physical action. It has also been suggested as explanatory of this change that the mother being itself a material in a state of decay by oxidation, it induces the same change in alcohol. This view receives support from the fact that alcohol vapour brought into contact with decaying wood is slowly converted into acetic acid. This assumption is not opposed to the action of atmospheric oxygen causing this change.

The concentration and temperature of a liquid have an important influence on the formation of acetic acid. The amount of alcohol in the liquid must not exceed 11 per cent., since acetification does not take place in liquids containing much alcohol; on the other hand the change takes place very slowly in liquids containing but very little alcohol. Usually, therefore, no liquid is used containing less than 2 or 3 per cent. of alcohol. The temperature must be kept above 20°, or even higher, in order to hasten the action, but it should not exceed 40°, otherwise alcohol may be carried off by evaporation.

Only such liquids as wine, beer, malt infusion, or beet-root juice, are employed for making vinegar, according to the old method, as these contain, in the form of albumenoids and various salts, a considerable quantity of nutriment for the fungoid growth.

Wine Vinegar.—In the manufacture of wine vinegar, as carried on in wine-producing districts, both sound wine and wine that has become sour are used. As the wine must be clear, it is necessary to filter or otherwise clarify muddy wine. White wine is quickly acetified, and old wine more quickly than new wine containing much sugar. Wine containing more than 11 per cent. of alcohol requires to be diluted. The oak casks called 'mothers,' which are employed in making vinegar, have a capacity varying between 25 and 100 gallons. They are bored at both ends so as to give free access to air in the space above the liquid contents, and each cask is provided with a hole for manipulation, emptying, etc. Small casks are preferable to those of large capacity, for the reason that a greater surface of liquid is exposed in several small casks than in one large one. The casks are filled one above another on a wooden stand in the fermenting chamber, where the temperature is maintained between 25° and 30°. As the heat generated by the conversion of the alcohol is not inconsiderable, great care is necessary in places where the casks are closely packed, and proper ventilation maintained.

At the commencement of the operation the casks are filled to one third of their capacity with old and previously-heated vinegar, and to this two or three gallons of wine are added. The mixture is allowed to stand for eight days, during which time the acetic fungi in the old vinegar convert the alcohol in the added wine to vinegar, and increase at the expense of the nutriment present in the wine. Another similar quantity of wine is then added, and this is repeated twice more at the same interval of time. Eight days after the last addition, vinegar, equal to the total quantity of wine added, is drawn off, and the same operation is repeated.

Occasionally it happens that without any visible cause the acetous fermentation gradually diminishes in a striking manner and almost entirely ceases. According to

Pasteur this is due to the presence of minute animalcules called vinegar eels, which consume the oxygen necessary to the development of the *Mycoderma aceti*. When this has proceeded so far that these animalcules rise to the surface of the liquid in the place of the mycoderma, the progress of the fermentation is arrested. The readiest method to overcome the difficulty is to empty the casks and refill with hot vinegar, whilst in many cases the same result can be obtained by adding stronger wine or by increasing the temperature.

In the usual course, every six or eight years the casks require to be emptied and purified from the large mass of dead fungi (mother of vinegar), tartar and other salts adhering to the bottoms and sides.

According to the Orleans method, originated by Pasteur, the wine, or other alcoholic liquid, is placed in a vat, together with vinegar fungi, obtained in a previous operation. The fungi rapidly spread over the surface when the liquid contains the necessary food, and at the same time acetic acid is formed by the oxidation of the alcohol. Fresh wine is added daily; and, when the acetification is over, the vinegar is drawn off. The fungi, after being washed, can be used for a fresh operation. A barrel of from 10 to 20 gallons capacity will daily turn out a gallon to a gallon and a quarter of vinegar. If dilute alcohol be used, the food of the fungus in the shape of alkaline and magnesian phosphates must be added. Breton-Laugier uses a mixture of vinegar and wine, and keeps it in barrels of about 27 gallons capacity, at a temperature of 25–50° C. with vinegar fungi. After eight to ten days the entire quantity is acetified.

Beer Vinegar.—Only soured beer is used for this purpose, since, on account of its containing hop extract, it is not generally suitable for vinegar making. As it is poor in alcohol some spirit is added, together with water in order to dilute the extractive constituents. Beer that has been made by surface fermentation, on account of it containing less hops, is more suitable than that made by bottom-fermented beer. The acetification of beer is carried out in a manner similar to the manufacture of wine vinegar.

Malt and Grain Vinegar.—The manufacture of vinegar from malt or grain is largely carried on in England. The wort is prepared from a light kiln-dried malt, or from a mixture of malt and grain, by the mashing process as described under the article Beer (p. 946), with the exception that the mash is neither boiled nor are hops added to it. The wort having been brought to the fermenting temperature, and allowed to ferment, is run into the vinegar casks, which are either placed in rooms or exposed in the open air. When the acetification is completed the vinegar is siphoned off as clear as possible into a wooden trough connected with the common reservoir. Before the vinegar is run into the store vats it must be made quite clear by being passed through suitable clarifying vats, which consist of large vessels provided with sieve bottoms covered with such materials as straw, wood shavings, or better with grape stalks.

Beet-root Vinegar.—Although the preparation of vinegar from this source is but recent a number of recipes are extant; but this method has not yet met with much favour. The juice obtained in the ordinary way, by grating and pressing, is used either crude or purified with tannic acid or lime (see p. 834), being subjected first to the alcoholic fermentation and afterwards to the acetic fermentation. It is then clarified by subsidence in vats or by filtration. Leplay's method consists in cutting beet roots into slices and setting up fermentation by immersing them in already fermenting beet-root juice. The sugar thus undergoes alcoholic fermentation in the cells of the roots, and upon exposure of the slices to air the alcohol very soon undergoes acetification. The vinegar can be either distilled with steam or by washing the fermented mass. To make vinegar from brandy by the old method the plan followed is the same as described for wine vinegar. The brandy, or spirit, is diluted with water until it contains only 6 or 7 per cent. of alcohol, then heated to 35° or 40°, and finally mixed in the fermenting vats with 'mother of vinegar,' the growth of which is sustained by adding partly fermented malt extract. The conversion of brandy into vinegar is now more frequently carried out by the quick process.

The Quick Vinegar Process.—The production of vinegar by this method has to a great extent superseded that of fermentation above described: it consists in exposing a weak alcoholic liquid to the action of atmospheric oxygen in such a manner as to present a very extended surface, and thus to accelerate the oxidation of the alcohol and its conversion into acetic acid. For this purpose the alcoholic liquid operated upon is made to flow continuously through a capacious vessel into which air is admitted so as to come into contact with the liquid to be converted into vinegar. It is important that an abundant supply of air should be passed into the vessel, because when the oxidation of the alcohol takes place slowly aldehyd is formed instead of acetic acid. and

on account of the great volatility of this substance considerable loss would be incurred by its escaping in the state of vapour. Part of the vessel in which this operation is carried out is therefore filled with some porous material, such as wood shavings, over the surface of which the alcoholic liquid is distributed, and thus brought more intimately into contact with the atmospheric air passing through the vessel. By this method it is possible, owing to the large surface exposure, to convert alcohol into acetic acid in three days, whilst by the old method it would take several weeks. The apparatus, represented by fig. 697, consists of a wooden cask, or vinegar generator, 6½ feet high by 3¼ feet in diameter, and slightly conical. A shelf (B B), perforated with small tapering holes, is fixed about 6 inches below the cover (A A) of the vat. The shelf rests on a beech-wood ring fixed inside the vat. In each hole is a piece of string 6 inches in length which half closes up the hole and is retained by a knot. This shelf is also provided with larger holes to contain glass or wooden tubes (C C C) to act as air vents. About 16 or 20 inches above the bottom of the tub is placed a second perforated shelf (D), also resting on a beech-wood ring, and 2 inches above it, at intervals so as to encircle the tube, ten to fifteen holes (E E) are made which have a downward inclination in order that the down falling liquor shall not leak from the tub. The space (F) between the two shelves is filled with shavings. The exit pipe (G) is placed 2 inches above the bottom of the tub and is bent like a siphon, but with the outer arm shorter than the inner one, so that the vinegar can only flow out to a certain level. A thermometer passing through the upper perforated shelf serves as a guide to the progress of the operation. A new generator, before being used, requires to be percolated for some time with hot old vinegar, until the shavings are completely saturated; then dilute spirit, containing 6 to 10 per cent. of alcohol, is added. The liquor flows through the holes partly plugged with twine in small and very finely divided drops, falling upon the shavings below, where, under the influence of the in-coming air and the vinegar ferment, the alcohol is oxidised, and it collects below the second perforated shelf. From the first cask the partly converted liquor is passed through a second one, and then through a third similarly constructed vessel; or, instead of this, one vessel can have the liquor passed thrice through it.

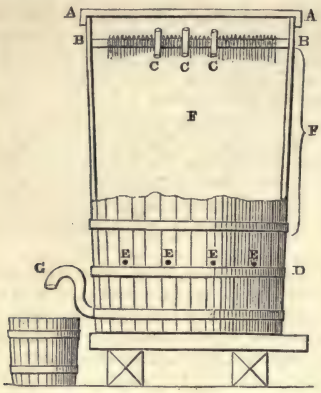


Fig. 697.

Should the acetification be incomplete after a third passage through the casks the operation must be repeated again.

Otto has proposed that, instead of adding the alcohol all at once, a part of it should be mixed with vinegar and passed once through the generator, then to pass through another portion of the alcohol, and to add the remainder after repeated percolations of the earlier portions. In this way less vinegar is required to be added to the alcohol.

Only about one-tenth, or at most one-fifth, of the oxygen in the air passing through the generator is absorbed in the oxidation of alcohol, and consequently a large quantity of air is discharged above, which causes considerable loss of alcohol and acetic acid vapour. Payen has proposed, therefore, to pass the escaping vapours through a worm condenser fitted to each generator; or to pass the air over copper turnings and form verdigris.

At the commencement of the process the temperature in the vinegar room is brought to 38° C., but as the operation progresses and the temperature rises in the generator, the heat is lowered to 20° or 23° C. The alcoholic liquid first used for the generator is heated to 50° to 52° C., but when the process is in full operation the temperature of the liquor is maintained between 26° and 27° C.

Payen describes a new method as carried out in the manufactory of Koelitz. In an enclosed chamber on an upper floor are placed fifty-four conical vessels provided with false bottoms. Each vessel is 4 feet high, has a width at the top of 4 feet, and at the bottom of 4 feet 10 inches; on the perforated bottom are placed fourteen horizontal layers of beech-wood shavings rolled in a spiral form and pressed together. Each spiral, held together by a cross band, measures about 8 inches by 6 inches in diameter, and is 2 inches high. Each layer contains forty-eight such spirals;

therefore the fourteen layers contain 672 spirals, and these, having twenty-eight twists and being one twenty-fifth of an inch thick, represent a total surface of about 42,800 square feet. The chamber is maintained at a temperature of 25° C. The alcoholic liquid to be acetified is prepared so as to contain about 7 per cent. by volume of alcohol, and it is passed through a kind of rose feeder from a vessel over the casks upon the beech-wood spirals; the oxidation which follows raises the temperature to 27°, and the liquor collects in the space under the perforated bottom completely converted into vinegar containing about 11 to 12 per cent. of acetic acid. In order to oxidise the alcohol a stream of air is passed through each generator by a wooden pipe at the bottom, and is conducted into a chimney common to the entire apparatus. By slowly allowing the mixture to flow over the beech shavings the acetification is finished in two hours, and by adding at such intervals about 10 pints of liquid containing 5 pints of 14 per cent. alcohol and 5 pints of 7 per cent. vinegar, a yield of upwards of 800 gallons in twenty-four hours can be obtained from fifty-four generators.

Mr. Singer has described a generator where the wood shavings are not used. The liquor flows continuously in a thin stream through vertical pipes upon eight channels placed some distance apart. Air has access to the pipes through slits at the lower part. The diameter of the apparatus is about 5 feet and the pipes number 138, each of which measures 21 inches in length and one-fifth of an inch in diameter.

Vinegar is conveniently tested by Otto's method with the acetometer, which is a graduated tube represented by fig. 698, of about 1 foot in length and ½ inch in diameter. From the bottom of the tube to $a = 1$ cubic centimetre or 1 gram, from a to $b = 5$ cubic centimetres or 5 grams, from b to $c = 5$ cubic centimetres or 5 grams, in all cases of water. Each division above c answers to 2·07 grams of ammonia solution of sp. gr. 1·369, and this quantity exactly saturates 0·1 gram of acetic acid. The tube is filled to a with litmus solution and from a to b with the vinegar under examination. If the vinegar is strong, only sufficient is taken to fill up to b, this diluted with water to c; in that case the result must be multiplied by two. The standard ammonia is added with frequent shaking until the red litmus tint is changed to the neutral tint. The number of divisions to which ammonia is added gives at once the percentage of acetic acid. For example, if ammonia has been added to the seventh division, then the quantity of acetic acid = 7 × 0·1 = 0·7 grams in 10 grams of the vinegar, or 7 per cent.



FIG. 698.

Instead of ammonia solution a 10 per cent. soda solution can be used equally well.

The older method, in which to a known quantity of vinegar solid carbonate of potash is added until the neutral tint is obtained, after boiling the liquid, gives less exact results. The same applies to the method of estimation by the loss occasioned by a weighed piece of carbonate of lime or marble when immersed in the vinegar. An equivalent quantity of carbonate of lime is dissolved by the acetic acid; 5 grams of carbonate of lime = 6 grams acetic acid.

As already mentioned the areometer is not suitable for acetic acid testing, as its specific gravity increases by adding water to a certain point, and then again diminishes.

Kieffer titrates the vinegar with a standard solution of ammonio-cupric sulphate until a precipitate ensues.

Other acids are frequently added to increase the strength of vinegar. This practice when carried out to a considerable extent is prejudicial to the health. The acids chiefly used for the purpose are sulphuric and tartaric acids, and, exceptionally, hydrochloric and nitric acids.

To detect sulphuric acid, a drop of baric chloride is added; if only a slight precipitate is formed, it would be due to the sulphates of the water used in the manufacture, but if a considerable precipitate is formed, free sulphuric acid must be tested for as follows. Some of the vinegar is mixed with a little starch, and distilled in a retort to one half its original volume. If free sulphuric acid is present, it converts the starch into sugar; and, on adding to the cold liquid iodine solution, the blue coloration characteristic of starch is not produced.

Tartaric acid is only to be tested for in wood vinegar, etc., as wine vinegar contains it naturally. The procedure is as follows:—The vinegar is evaporated on the water to a syrup; the residue mixed with a very little water and a small quantity of ferric chloride, and boiled; caustic potash is then added until the liquid has an alkaline reaction, and the whole is filtered. If upon sulphuretted hydrogen being added to the filtrate, it gives a black precipitate, the presence of tartaric acid is indicated.

To test for hydrochloric acid, some of the vinegar is distilled in a retort. If the distil-

late tested with nitrate of silver solution gives a precipitate of chloride of silver, the presence of free hydrochloric acid is indicated. Nitric acid is detected by neutralising with carbonate of soda, evaporating to dryness, and boiling with copper foil and sulphuric acid; a disengagement of red fumes of nitrous acid gives evidence of the presence of nitric acid.

Vinegar is frequently mixed with cayenne pepper and other hot spices in order to give it a pungent or aromatic taste. These are easily discovered by their taste when the acid of the vinegar is neutralised with carbonate of soda. The vinegar is sometimes contaminated with poisonous metals derived from the vessels used in the manufacture, as lead, copper, tin, and zinc, all of which can be detected by their precipitate with sulphuretted hydrogen.

Uses.—Besides the domestic uses of acetic acid in the form of vinegar, this substance is of importance in the arts. It is employed for the preparation of the salts called acetates, such as calcium acetate, into which form the crude acetic acid obtained by the distillation of wood is generally converted, either for convenience of transport or as a first stage of purification. This salt is also used in the preparation of some other acetates, such as aluminum acetate and sodium acetate, by mixing a solution with aluminum sulphate or sodium sulphate sufficient to separate the calcium in the form of sulphate. An addition of acetic acid of 7 per cent. strength is made to dilute wine vinegar in order to strengthen it and to render it more durable. Dilute acetic acid has also been substituted for wine vinegar, some dilute wine being added to supply the necessary aroma. A great quantity of acetic acid is used in the manufacture of white lead (see p. 393), and in the preparation of aniline from nitro-benzol. It is also extensively used in chemical laboratories, and for medicinal purposes.

TEA, COFFEE, COCOA, ETC.

The products of various plants, known by the above names, are extensively used in various countries as articles of food, and from a chemical point of view they present many features of resemblance in composition.

Tea consists of the dried leaves of several varieties of *Thea sinensis*, a plant indigenous in China, Japan, and the northern parts of India, where it is extensively cultivated. The tea plant appears to be capable of flourishing in all latitudes between the equator and 40°, and its cultivation has been introduced upon the southern declivities of the Himalayas in British India, in Java, Western Africa, Brazil and Madeira.

The difference between black tea and green tea was formerly supposed to be due to a difference in the plants from which the leaves were obtained, but it has now been ascertained that green tea is prepared from young leaves by a rapid process of drying, whereas the black tea consists of older leaves which are allowed to lie in heaps for some time after having been gathered, and to undergo a kind of fermentation or change somewhat similar to that taking place in making hay.

Coffee beans are the perisperms or endosperms of the fruit of the coffee tree (*Coffea arabica*, Fam. Rubiaceæ), deprived of the pericarp. The horny mass of the beans consists of thick-walled pitted cells. When treated with sulphuric acid and iodine, the cellulose assumes a peculiar blue colour; by prolonged contact the cell walls dissolve to a mucilaginous liquid. The remaining parts of the bean when similarly treated assume an orange tint. The bean may be considered as consisting of: 1. Cuticle surrounding the surface of the perisperm and permeated with fat, nitrogenous substances, and ash constituents; 2. Spongy nitrogenous substances which, together with oleaginous substances, fill up the cells of the epidermis; 3. Granular fatty masses filling the innermost cells; 4. The membranes impregnated with albumin filling the intercellular spaces.

Cocoa consists of the kernels of the beans or seeds of the *Theobroma Cacao*, a tree indigenous in the West Indies and Central America, and growing extensively in Mexico, Caraccas and Demerara. It is cultivated in the Mauritius and Bourbon; the roasted kernels are either simply ground and sometimes pressed to separate part of the fat they contain, or they are ground with sugar into a paste which is called chocolate, and is sometimes flavoured with vanilla.

Paraguay tea or *Maté* consists of the dried leaves of the *Ilex Paraguayensis*, a kind of holly, growing in Paraguay and Brazil, where it is known by the name of yerba maté.

Guaraná is a substance that comes from South America, where it is prepared by the Indians; it consists of a hard paste prepared from the ground and slightly roasted seeds of *Paullinia sorbilis*. It is used by the natives much in the same way as tea and coffee are used in other countries.

The peculiar effect produced by tea or coffee upon the human organism is the result of a number of their constituents, among the chief of which are the substances called thein or caffein ($C_8H_{10}N_4O_2$) according to the source from which it is obtained, and some ethereal oils which are chiefly produced in the roasting of the beans. Probably this is also the case with regard to maté and guaraná, the former of which contains, according to Byasson, nearly 2 per cent. of thein, while the latter contains as much as 4 or 5 per cent. Cacao beans contain a similar substance called theobromin ($C_7H_8N_4O_2$).

Caffein occurs in tea leaves and in the coffee bean, partly in the free state, but, in the latter case, according to Payen's researches, chiefly in combination with tannic acid.

In order to prepare caffein from coffee, the beans are first dried at 100° until sufficiently brittle to be powdered. The powder is then treated with ether in a percolator, until the ether passing through no longer leaves a stain upon paper. The ethereal solution contains the entire amount of fat and caffein present in the beans. The ether is distilled off, the residue boiled up with several quantities of fresh water, and the aqueous solution of caffein separated by filtration from the insoluble fat

The aqueous solution is evaporated to dryness in a water bath, and the residue boiled with absolute alcohol so long as anything is dissolved. On cooling the alcoholic solution the caffein crystallises out.

Caffein in a pure state forms white silky needles, soluble in 90 to 100 parts of cold water; it is much more soluble in hot water, and sparingly soluble in alcohol or ether. The crystals obtained from aqueous solutions contain water of crystallisation, which is given off entirely at a temperature of 100°. At a temperature somewhat higher the caffein begins to volatilise. At 234° to 235° caffein melts without decomposing, boils at 384°, and sublimes, the vapour condensing upon cooling in hair-shaped needles. The caffein crystallised from water has the formula:

$$C_8H_{10}N_4O_2 + H_2O.$$

Caffein is soluble in acids, but enters into combination with very few. Upon evaporating the aqueous solutions, in most cases pure caffein crystallises out. Caffein forms a stable compound with hydrochloric acid, which compound is prepared by dissolving caffein in the concentrated acid, evaporating and crystallising; from weak aqueous solutions of caffein in hydrochloric acid the caffein crystallises out in the free state upon evaporating the liquid. The hydrochlorate yields double salts with the chlorides of platinum, gold, and mercury. Caffein itself enters into combination with silver nitrate and mercury cyanide. The so-called caffein citrate used in pharmacy is not a true compound, but merely a mixture of citric acid and caffein.

Both tea and coffee contain astringent substances belonging to the class of tannins. The tannin of tea leaves gives a blue-black precipitate with iron salts, and according to Stenhouse it is distinct from the tannin of nut galls. The tannin of the coffee berry colours ferric salts green, and does not precipitate ferrous salts. When exposed to the air in contact with alkalies it gradually acquires a brilliant green colour, and is converted into a substance called viridic acid.

According to Payen, caffein exists in coffee partly in the state of combination with tannic acid and potash. To obtain this salt, the coffee beans that have been exhausted with ether are treated with alcohol of 60 per cent., the solution evaporated to a syrupy consistency, and the residue mixed with three times its volume of alcohol of 85 per cent. The liquid separates into two layers, the lower one being a sticky liquid of considerable density, above which floats a light mobile liquid. The latter contains the chief quantity of the salt in question; it is poured off from the heavier liquid, and the residue shaken up with alcohol of 85 per cent., so long as a drop of the liquid, when mixed with a little water and heated, gives a greenish colour with ammonia. The total quantity of alcohol that has been used is then distilled off, and there remains a residue of syrupy consistence, which is then mixed with a quarter of its volume of alcohol of 90 per cent. After a lapse of twenty-four to forty-eight hours, the whole solidifies to a crystalline mass, which is first washed upon a filter with cold alcohol of 65 per cent., and then re-crystallised several times from boiling alcohol, so as to obtain it in a state of purity. In the preparation of this salt, great care is required to keep it out of contact with vapours of ammonia, which is effected by placing the solutions over vessels containing sulphuric acid, the whole being protected by a glass bell jar; in like manner the water used for diluting the alcohol must be entirely free from ammonia, since mere traces of ammonia exert a decomposing action upon the salt.

Potassium and caffein caffetannate possesses electrical qualities in a high degree. Upon rubbing crystals of the salt, previously dried at 100°, upon a piece of warm paper, and bringing a blade of a knife in contact with them, they adhere to the blade in little groups. The salt admits of being heated to 150° without undergoing any change; it melts at 185°, assuming a fine yellow colour, begins to boil, swells up to five and six times its original volume, and is converted into a porous brittle yellow mass. At 230° it becomes brown and is partly decomposed. The vapour evolved at this temperature yields crystals of caffein by condensation. By further heating the substance becomes dark brown, again melts, evolving alkaline vapour, and finally swells up to twenty times its original volume, leaving a light iridescent charcoal. The increase in volume observed in roasting coffee beans is due to the alteration in this compound.

The double salt of potassium and caffein caffetannate is scarcely soluble in absolute alcohol. From hot alcohol of 95 per cent. it crystallises in prisms radiating from a common centre. The salt is more readily soluble in hot alcohol of 85 per cent., from which it crystallises out abundantly upon cooling. The solubility of the salt increases with the dilution of the alcohol. The salt is easily soluble in water, a hot concentrated solution solidifying to a kind of magma upon cooling. An aqueous solution of potassium and caffein caffetannate decomposes in contact with atmospheric air, assuming first a yellow and afterwards a brownish-green tint.

Upon slightly warming the salt with potash, the crystals assume a hue varying between vermilion and orange. At a higher temperature they melt, turn yellow, evolve ammoniacal vapour, then become brown and decompose. Heated with concentrated sulphuric acid the crystals assume an intense violet colour, and become covered with an iridescent film. Concentrated hydrochloric acid produces the same effect, and nitric acid produces an orange-yellow colour. Lead acetate produces in aqueous solutions of potassium and caffein caffetannate a flocculent pale yellowish-green precipitate. With basic lead acetate a similar precipitate is formed, but of a yellow colour. Neutral silver nitrate has no effect upon aqueous solutions of the salt, while the slightest trace of ammoniacal silver nitrate produces a cloudiness, metallic silver separating out on the sides of the test glass.

In order to separate the caffein from this compound, an aqueous solution is mixed with a quantity of sulphuric acid equivalent to the potash it contains, and evaporated to dryness with powdered marble to neutralise any possible excess of sulphuric acid. From the residue, tannate of caffein is dissolved out with alcohol, and basic lead acetate added to precipitate the tannic acid, and the precipitate is washed with hot alcohol, from which the caffein crystallises out on cooling.

Caffetannic acid is obtained by decomposing the above-mentioned lead precipitate with sulphuretted hydrogen; upon evaporating the solution, the caffetannic acid separates in small irregular crystals which are washed with cold absolute alcohol. They are white, sparingly soluble in absolute alcohol, more readily in dilute alcohol, and very soluble in water. A hot saturated aqueous solution of caffetannic acid crystallises slowly upon cooling, forming microscopic prisms grouped in little bundles round a common centre; after standing for three or four weeks the prisms unite, forming granules 1 to 2 mm. in diameter. A solution of caffetannic acid has a strong acid reaction. The crystallised acid melts when heated, turns yellow, boils, and leaves light porous brilliant charcoal. Its composition is represented by the formula $C_{14}H_{16}O_7$.

Coffee beans contain about 12 per cent. of fat, and the kernels of the cacao nuts contain from 52 to 53 per cent. of a peculiar fat, which is used in pharmacy under the name of cacao butter.

The Aromatic Oils.—Although the aromatic constituents of articles of food are devoid of direct nourishing power, they are nevertheless of importance, owing to the effect produced by them upon the nervous system, which latter in its turn supports the processes of digestion and assimilation. Among these aromatic substances are the volatile oils which exist in the coffee bean, or are formed during the roasting. The aroma of coffee may be isolated by distillation; the amount, however, is so small that very little is known of it beyond the fact that it is soluble in water.

The volatile oil of tea may be obtained either by distillation or by extraction with ether. It is yellow, lighter than water, has the smell and taste of tea, and a powerful stimulating action.

The kernels of the cacao nuts or beans contain, in addition to the fat above mentioned, about 17 per cent. of albuminous substance, 11 per cent. of starch, 8 per cent. of gum or mucilage, together with theobromine and a bitter substance. The beans when fresh gathered are either dried at once or after being subjected to a kind of fermentation or curing, by means of which the natural bitterness is removed. They are slightly roasted before being ground, and in this operation the aroma is developed, while part of the starch is converted into dextrin. In grinding the roasted kernels into the paste that is known as flake cocoa, or rock cocoa, starch and sugar are sometimes added in considerable proportions, and chocolate always contains admixtures of this kind, as well as flavouring substances, such as vanilla. In making the better kinds of cocoa or chocolate, the husks of the beans are separated; but in the inferior kinds they are sometimes ground up together with the kernels.

Characters of different kinds of Tea and Coffee.—The differences in quality of the tea and coffee met with in commerce are due to the plant from which they are obtained, partly also to the differences in soil, climate, cultivation, and harvesting.

The quality of tea depends very much on the season at which the leaves are picked, the mode in which they are prepared, and the district where they are grown, and it is chiefly to these conditions that the distinction between the varieties known as Bohea, Congou, Souchong, Pekoe, Hyson, etc., is to be ascribed. The amount of substance extracted by water varies considerably, as shown by the following average results obtained by Stenhouse:—

	Per cent.
Dry black tea	43·2
Dry green tea	47·1
Black tea, as met with in commerce	38·4
Green tea, as met with in commerce	43·4

The average percentage composition of dried tea is as follows, according to Mulder:

	Chinese tea		Java tea	
	Hyson	Congou	Hyson	Congou
Volatile oil	0·79	0·60	0·98	0·65
Chlorophyll	2·22	1·84	3·24	1·28
Wax	0·28	—	0·32	—
Resin	2·22	3·64	1·64	2·44
Gum	8·56	7·28	12·20	11·08
Tannin	17·80	12·88	17·56	14·80
Thein	0·43	0·46	0·60	0·65
Extractive	22·80	19·88	21·68	18·64
	—	1·48	—	1·64
Extracted by hydrochloric acid	23·60	19·12	20·36	18·24
Albuminous substance	3·00	2·80	3·64	1·28
Woody fibre	17·08	28·82	18·20	27·00
Ash	5·56	5·24	4·76	5·36
	104·34	104·04	105·18	103·06

The Martinique coffee beans are generally large, and of a greenish colour with flattened surface; individual beans have sometimes an elliptic shape, owing to the non-fructification of an ovule; sometimes, but less often, beans having a somewhat angular form are found, produced by the mutual pressure during growth of three fructified ovules in the same fruit.

Mocha coffee differs from the former, inasmuch as the beans have a yellowish grey colour, and are smaller and less regular in shape. Owing to the development of two beans in a fruit, one side is in most cases flattened, only a few berries being rounded; as occurs when only one ovule is fructified. Mocha coffee differs further from all other kinds of coffee in being richer in fat, the amount being as much as 13 per cent. The fat has a yellowish colour, and is softer than that found in other sorts of coffee. Payen found in it two distinct kinds of fat, with different melting points. The fat retains the aromatic constituents with great energy; the quantity of which latter constituents is relatively greater in Mocha coffee than in other sorts.

The fat of Martinique coffee is of a darker colour, of greater consistency, and can be separated into four distinct fats, having melting points about 5°, 20°, 50°, and 90°, the latter being very similar to the wax found in the leaves.

The occurrence of the wax-like substance and the green colour are probably due to the time at which the berries are collected, and the shelling of the pods. Upon removing the fleshy part of the fruit while it is filled with sap, the perisperm being exposed to the air is altered by the action of oxygen; the caffetannic acid becomes green, and the fat substances are altered, while the soluble substances to which the aroma is due, may be decomposed and volatilise. For this reason it would be better—especially for inferior sorts of coffee—to allow the fruit to become as ripe as possible, before gathering and shelling them.

The average percentage composition of coffee berries is as follows:—

Cellulose	34
Moisture	12
Fat	10 to 13
Glucose, dextrin, and undetermined acid	15·5
Legumin, casein (gluten ?)	10
Potassium and caffein caffetannate	3·5 to 5·0
Nitrogenous substance	3·0
Free caffein	0·8
Solid essential oil, insoluble in water	0·001
Two different aromatic oils, soluble in water	0·002
Ash constituents	6·697

Coffee is always roasted before being used, and in this operation it undergoes considerable alteration, losing about 12 or 18 per cent. of its weight and becoming darker coloured according to the degree of heat employed in the roasting. The beans also lose their toughness, swell up and become so brittle that they can be readily ground to powder, while at the same time an agreeable aroma is developed. In roasting

coffee the heat requires to be carefully regulated, and the beans must be kept in motion so that all of them are equally heated. For this purpose rotating vessels of a cylindrical or globular shape and made of sheet iron are generally employed.

Uses.—Although tea, coffee, and cocoa or chocolate, are articles of daily consumption, and although their use extends over all parts of the earth, so that they may be almost considered as necessary articles of food, still their actual value as food material is but slight, and the nutritive effects produced by them bear no proportion to the quantity consumed.

As regards the physiological effects of coffee, it was at one time supposed that the use of coffee might reduce the consumption of albuminous constituents in the body, but this has been shown by the researches of Voit to be entirely erroneous.

The influence of coffee is chiefly to be ascribed to caffein, which has an energetic action on the system, in small doses as a stimulant exciting the imagination, and in large doses giddiness, headache, and even delirium and convulsions. Animals have been poisoned with caffein under precisely the same symptoms that are produced by strychnine.

A certain amount of stimulus to the nervous system seems to be indispensable to the human economy. A variety of different substances are consumed for this purpose, for instance, wine, spirit, tobacco, coffee, tea, broth, opium, haschisch, etc., every nation having its own peculiar stimulant, which, although not directly nutritive, has considerable influence on the general condition of the system. Coffee is one of the most important materials of this class.

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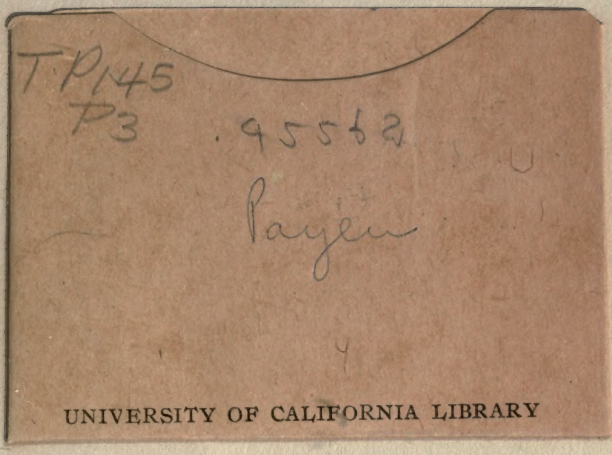
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